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ANALYTICAL APPROACH TO THE CHARACTERIZATION OF MILITARY LUBRICANTS

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under Contract to

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As an integral part of the Army's overall power train lubrication research effort, analytical/instrumental methods continue to be developed for use in determining compositional characteristics of new lubricants and to detect unusual contaminants in <i>new</i> and <i>used</i> lubricants. Included among the various types of instruments being used in this work to characterize lubricants are: gas chromatography (GC), high performance liquid chromatography (reversed-phase, adsorption, gel-permeation), and spectrophotography (see back)		

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metry (IR, UV, AA, XRF). Methods to separate lubricants into component parts according to chemical types in order to simplify the subsequent analysis and identification of the component parts have been applied with favorable results. Technology has progressed to where it is now possible to qualitatively analyze and quantitate the major base stock components in hybrid lubricant blends, i.e., those in which synthetic hydrocarbons, esters, and mineral oil-based components are blended together. The synthetic hydrocarbon and alkyl diester portions of hybrid synthetic lubricants can be separated and analyzed by infrared spectroscopy, gas chromatography, and gel permeation chromatography. The ester fractions are large and pure enough to permit further study by hydrolysis and derivatization to determine exact composition of the acidic and alcoholic components. Characterization of lubricants to include additives is not yet complete. Ultimate refinements of this approach will provide the detailed compositional information needed to define base stock characterization, develop correlation of lubricant component to equipment performance, and identify sources of *new, used, synthetic and re-refined lubricants*, power train and hydraulic fluids.

FOREWORD

The work reported herein was as an integral part of the Army's on-going applied lubrication research program. It was conducted at the U.S. Army Fuels and Lubricants Research Laboratory (USAFLRL) located at Southwest Research Institute, San Antonio, Texas, under contract nos. DAAK02-73-C-0221 and DAAG53-76-C-0003 during the period 1 March 1973 through 1 March 1976. The contract monitor was Mr. F.W. Schaekel, USAMERADCOM, DRXFB-GL, Ft. Belvoir, Virginia.

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INTRODUCTION

The U.S. Government operates the largest single ground-vehicle fleet in the world, including materials handling and automotive support equipment. The U.S. Army has the custodial responsibility for the principal automotive engine lubricant specifications^{(1,2)*} under which the Federal Government purchases engine oils for its civilian and military ground vehicle fleet. In addition to this enormous engine oil responsibility, the Army also develops and maintains specifications for the procurement of gear oils,⁽³⁾ arctic engine^(4,5) and arctic gear oils,⁽⁶⁾ and hydraulic oils,^(7,8) for use in DOD ground powered military equipment, and in Army aircraft systems. Knowledge of lubricant nature, product quality, basic composition, and performance characteristics are tantamount to the Army writing the most meaningful specifications for government product procurement purposes. Product quality control, quality assurance, and used-lubricant analyses are three of the critical lubricant functional aspects in which state-of-the-art chemical analysis must be applied if the best interests of the government as a *lubricant end-user* are to be satisfied.

Many routine chemical analyses developed in industry and government are directly applicable to certain of the lubricants the government uses in *non-combat* ground-vehicle service or support equipment (i.e., purchased under specification MIL-L-46152⁽²⁾). However, the requirements and needs of the Army and DOD ground-powered combat/tactical fleet and support equipment are *entirely different* from those in the civilian and non-combat sector. For example, one specification⁽¹⁾ lubricant is designed to satisfy a wide variety of engine types operating under varying conditions, unique to the military. Specific severe operating conditions include: *frequent long* periods of engine idling, short vehicle trips, or engine shut-down; unintentional or inadvertent use of wrong specification products; mixing of several different suppliers' products and viscosity grades (qualified under the *same* specification) in many engines, such that when there is an unusual problem, it becomes difficult to identify the specific lubricant(s) being used; and, the widest environmental temperature and climatic variations including *frequent trips* into sandy, dusty and snowy areas. To properly understand the nature of today's complex lubricants, it has become *necessary* for the Army to *develop and use more extensive analytical methods*. This has provided a basis for the *characterization* of the many different lubricants or *combinations* of lubricants used in fielded equipment. The current work was undertaken as an integral part of the Army's on-going applied lubrication research program aimed at the development of *improved* lubricants which will enable the Army to *reduce* the number of supply items and their qualification and procurement costs, reduce maintenance costs, and elevate the degree of equipment readiness. This report documents the analytical approaches to the characterization of military lubricants and provides examples thereof.

*Superscript numbers in parentheses refer to references at end of report.

BACKGROUND

Up until the early 1960's, the U.S. Army procured and used relatively simple lubricants compared with those materials being offered as a result of the modern lubricant formulation technology of the 1970's. It was common place for the Army to purchase single grade, *conventionally formulated* mineral oils of variable quality level depending on the performance requirements of the equipment in which the lubricants were to be used.

In the mid-1960's the Army recognized the benefits of using multi-viscosity grade engine oils and quickly adapted these oils⁽⁹⁾ for *non-combat* type vehicles (i.e., GSA Interagency motor pool sedans and pickup trucks; U.S. Postal Service trucks and sedans; and DOD commercial trucks and sedans). These multigrade oils, with their high molecular weight polymers added for high temperature thickening purposes, introduced the first of a series of complex problems to the government. This was due to the nature of the polymeric thickening material (generally referred to as a *viscosity index improver*). While industry and the civilian sector had been using these multigraded oils for a *decade* or more, the fact remained that the government was only beginning to purchase these types of oils in the mid-1960's. Viscosity index improvers are high molecular weight straight-chain/cross linked polymeric materials which undergo varying degrees of shear degradation in service and lose some (or all) of the viscosity improvement capability they are intended to impart to the finished lubricant. From an analytical standpoint, these materials present problems of identification (i.e., polar and non-polar blends) and separation, because of the critical solubility of the polymeric improvers, particularly if the lubricant is a used sample and possibly was mixed with another supplier's oil in the field.

Lubricant formulation technology has continued to advance (and become more complicated) since the mid-1960's, at which time the Army turned to synthetic-based arctic engine oils. The difficult requirement of low temperature fluidity coupled with good high-temperature performance in modern high-output diesel engines necessitated the development^(10,11) of a new arctic engine oil specification,^(4,5) designed around the use of synthetic lubricants as *problem solvers*. More recently, the 1973 Middle East oil embargo and the consequent advent of so-called *long-life* or *extended drain* and *no-drain* synthetic crankcase lubricants⁽¹²⁻¹⁵⁾ has required the Army to intensify their chemical analysis research development for the purposes of lubricant characterization as outlined above.

In earlier reports⁽¹⁶⁻¹⁸⁾ the properties and physical performance characteristics of many synthetic and mineral-based lubricants were presented and discussed. It is the intention of the current report to document the Army's capability for the chemical characterization of lubricants as of this point in time, with special emphasis on lubricant base stock. However the recommendations advanced at the end of this report clearly state that more work needs to be done, and it is expected that future interim reports will discuss these aspects of the program.

TECHNICAL PROGRAM

Lubricants

Modern lubricants are complex chemical mixtures containing one or more base-stock (major) components, and several additives that allow the finished lubricant to perform its function in an engine or other power flow system. The lubricant base-stock usually contains either:

- (a) mineral oil (solvent neutrals, pale oils, bright stocks, etc.),
- (b) synthetic hydrocarbon(s) (polyalpha olefins, polyalkylbenzenes, etc.),
- (c) synthetic organic compounds other than hydrocarbons (mono-, di-, tri- and tetra-esters, ethers, phosphate esters, polyol esters, polyethers, silicones, etc.), or
- (d) a combination of the above.

Similarly, the additive package in a finished lubricant has several constituents, usually including detergent; dispersant; anti-oxidant; antiwear; extreme pressure additive; and possibly a viscosity index improver polymer. While some components may exhibit multifunctional properties (improve more than one function of the lubricant) the number of major constituents of a lubricant may be large indeed.

Table 1 presents physical properties and composition data for the lubricants used in this study. The products are divided into two groups: Qualified/Candidate Military Lubricants, and Commercial Synthetic Lubricants.* The arctic lubricants are diesters, synthesized hydrocarbons or *hybrid* blends of each which have demonstrated good performance in laboratory tests and field Army arctic operations since 1967^(4,11). Also included in Table 1 are synthetic-based lubricants already qualified to MIL-L-46152 and a representative collection of current-generation commercial synthetics intended for extended-drain operation in commercial fleet vehicles and private passenger cars for periods of roughly 25,000-50,000 miles⁽¹²⁻¹⁵⁾. In the current programs, this latter group of lubricants are referred to as the *Commercial Extended-Drain Oils*. Note from the data in Table 1, "that the additive package makeup for the commercial *extended-drain* lubricants is quite close to many of the qualified/candidate military oils (synthetic and mineral-oil based). Also, the physical properties of the commercial oils do not differ radically."⁽¹⁶⁾

Analytical Approach

Data such as those contained in Table 1 are commonly used to describe lubricants. More detailed compositional information is generally needed to define base stock character, correlate base stock component type to performance, and identify the source of new, used, synthetic and re-refined lubricants, power train and hydraulic fluids.

*Two military lubricants (AL-3776 and AL-5075) are also commercial products.

TABLE 1. PHYSICAL PROPERTIES AND COMPOSITION OF TEST LUBRICANTS
(Note: Refer to Reference No. 16 for analytical methods for properties and composition.)

Lubricant Code No.	Qualified/Candidate Military Oils										Commercial "Extended-Drain" Oils							
	AL-5850	AL-5851	AL-5849	AL-3776	AL-5075	AL-5140	AL-4152	AL-4640	AL-5096	AL-5680	AL-5594*	AL-5604*	AL-5074	AL-5670	AL-5671	AL-5723	AL-5724	AL-571
Type	Mineral	Syn	Mineral	Syn	Syn	Syn	Mineral	Mineral	Syn	Syn	Syn	Syn	Syn	Syn	Syn	Syn	Syn	Syn
SAE viscosity grade	30	10W-30	OE/HDO-30	5W-20	5W-20	5W-20	OE-10	OE-30	5W-20	10W-40	N/A	N/A	N/A	10W-50	10W-40	10W-40	10W-40	10W-40
Description	N/A	N/A	SE/CD MIL-L-46152 MIL-L-2104C	CC Arctic	CC Arctic	CC Arctic	CC MIL-L-2104B	CC MIL-L-2104B	CD Arctic	SE/CC MIL-L-46152	N/A FA PD-5136	N/A FA PD-5136	N/A MIL-H-6083	SE None	CD None	SE/CD None	SE/CD None	SE None
SAE J183a Military	DEF-2101D	Unk																
Properties																		
Vis at 98.9°C, cSt	13.1	11.01	12.42	6.13	6.15	6.52	5.80	11.78	5.81	14.78	3.80	3.80	ND	20.99	15.48	14.57	14.60	15.70
Vis at 37.8°C, cSt	132.8	71.1	122.0	28.64	29.39	35.08	37.26	115.38	29.45	89.69	16.84	16.88	14.5	127.06	93.93	102.4	85.20	94.33
Viscosity index	100	156	101	214	180	153	103	98	153	183	131	ND	ND	203	188	133	144	189
Acid, meq/g	2.75	3.51	3.49	0.05	0.22	2.04	1.82	1.71	2.49	2.59	ND	ND	ND	1.40	3.08	5.86	1.54	1.79
Base, meq/g	8.69	4.86	4.74	6.40	7.77	8.04	3.82	4.72	7.97	8.60	ND	ND	ND	7.49	9.72	9.16	2.17	6.93
Flash point, °C	249	238	243	249	244	227	221	248	243	241	218	238	104	238	238	204	227	202
Pour point, °C	-7	-43	-18	-65	-57	-54	-23	-15	-54	40	ND	ND	ND	-40	-43	-32	-35	-43
API gravity at 15.6°C	26.1	25.7	27.3	21.1	21.2	23.5	30.6	ND	23.5	22.0	33.6	34.4	32.9	22.2	21.4	22.6	21.9	22.1
Composition, % wt																		
Sulfur	1.25	0.84	0.44	0.03	0.05	0.17	0.16	0.24	0.35	0.26	0.115	0.06	0.185	0.26	0.43	0.69	0.20	0.33
Phosphorus	0.105	0.119	0.086	0.012	0.01	0.08	0.10	0.095	0.09	0.10	0.20	0.10	ND	0.07	0.10	0.12	0.08	0.074
Barium	<0.005	<0.005	<0.005	0.88	0.84	0.004	0.52	0.25	<0.005	0.001	0.25	0.11	0.47	<0.001	<0.001	<0.001	<0.001	<0.001
Calcium	0.35	0.212	0.225	0.001	0.0005	0.25	0.017	<0.001	0.32	0.26	ND	ND	<0.001	0.15	0.28	0.32	0.23	0.14
Zinc	0.110	0.106	0.105	0.001	0.001	0.09	0.09	0.08	0.11	0.11	ND	ND	<0.001	0.08	0.11	0.19	0.11	0.08
Sodium	0.019	<0.001	0.006	ND	0.0012	0.0003	ND	ND	<0.004	0.01	ND	ND	ND	0.0008	0.003	0.002	0.02	0.0001
Sulfated Ash	1.20	0.91	0.94	ND	1.53	0.75	1.14	1.05	1.13	1.05	ND	0.22†	ND	0.67	1.25	1.58	0.90	0.65
Carbon Residue	1.28	1.10	1.18	1.56	1.39	0.96	1.16	1.05	ND	1.10	ND	ND	ND	0.76	1.46	1.96	0.94	0.76

*Frankford Arsenal Purchase Description 5136, Fire Resistant Hydraulic Fluid

Syn—Synthetic

N/A—Not Applicable

Unk—Unknown

ND—Not Determined

† Total Ash

As an integral part of the Army's power train lubrication research effort, analytical/instrumental methods have continued to be developed and applied to determine the composition of new lubricants and to detect unusual contaminants in new and used lubricants. To provide detailed analysis of these complex chemical mixtures prior separation is generally required to obtain analyzable simple systems. The analytical approach outlined in Figure 1 deals with the *sequential* separation, identification and measurement of components of mineral oil, synthetic hydrocarbon, polyalkylated benzene, and ester-based lubricants. This approach proposes no new art but places emphasis on the utilization of existing methods in a logical sequence as a guide to generate useful information about lubricant composition.

DISCUSSION OF ANALYTICAL CHARACTERIZATION METHODS AND RESULTS

A number of analytical instruments and separation methods are referred to in Figure 1 for the characterization of lubricants. The utility, applications, and resulting data produced by the application of these techniques are discussed best when segregated into specific analytical chemistry groups: (1) Spectroscopic methods, (2) High Performance Liquid Chromatography, (3) Chemical Hydrolysis of Diesters, and (4) Gas Chromatography.

Spectroscopic Methods

Infrared Spectrophotometry

When an unknown lubricant is submitted for analysis, first an infrared (IR) spectrum is obtained. Application of IR spectroscopy is useful because it allows one:

- to retain a permanent record of a given oil formulation that will serve as a basis for the detection of possible deviation from the originally approved formulation;
- to determine the nature of base-stock (e.g., mineral oil, ester type or polyalkylated benzene);
- to detect the presence of certain additives;
- to detect the presence of oxidation products (if acrylate-type VI improvers are not present and/or corrected for) in used oils; and
- to detect certain types of vehicle equipment failure, e.g., the leakage of ethylene glycol from the cooling system into the lubricating oil.

Some characteristic (diagnostic) IR wavelengths used in oil analysis are:

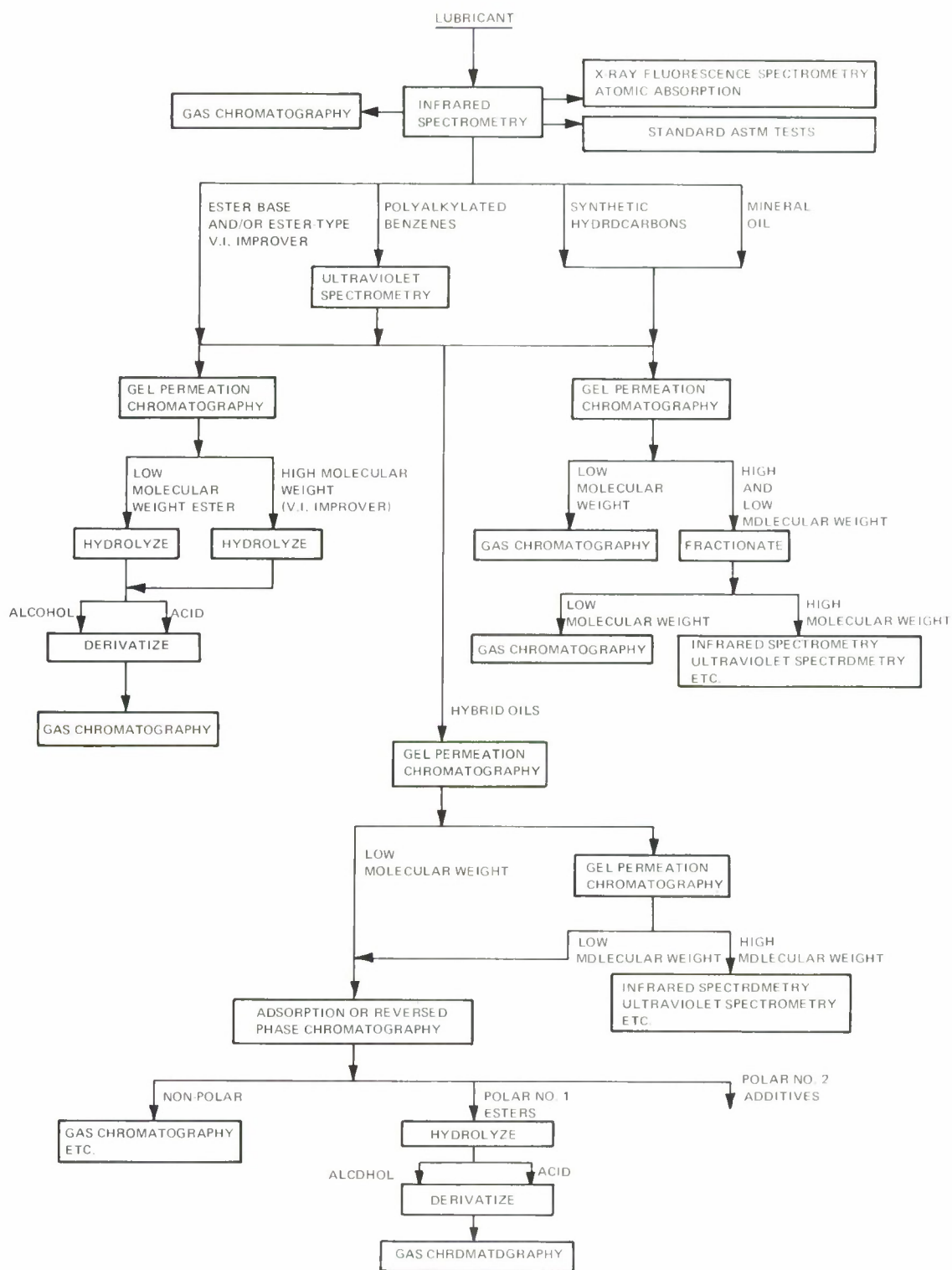


FIGURE 1. ANALYTICAL APPROACH TO THE CHARACTERIZATION OF LUBRICANTS

<u>Wavelength, μm</u>	<u>Structure or Vibrational Mode Producing IR Absorption</u>
2.8 - 2.9	OH stretching (e.g., glycols, phenols)
2.9 - 3.0	NH stretching (e.g., amines)
3.4 - 3.6	CH stretching (e.g., mineral oils)
5.8 - 5.9	C = O stretching (e.g., esters, some oxidation products)
8.0 - 8.5	SO ₂ stretching (e.g., sulfonates)
8.4 - 8.6	C-O stretching (e.g., esters, ethers)
9.8 - 10.4	P-O-C (e.g., dialkyldithiophosphates)
3.2 - 3.4	Aromatic C-H
11 - 14	Aromatic C-H

A cursory IR spectrum of an oil, therefore, provides a wealth of information that is also used as a guide in the selection of the proper subsequent analytical methods.

The IR spectrum given in Figure 2 provides a preliminary identification of the components contained in this mineral oil based finished lubricant. The IR spectrum given in Figure 3 provides a preliminary identification of the components in this ester containing "mineral oil" (hydrocarbon) based lubricant.

Additionally, quantitative determinations can be made by the "method of additions" for an ester containing lubricant when the particular ester has been identified and is available for this method.

Ultraviolet Spectrophotometry

This analytical method is used only to a limited extent in direct oil analysis for the qualitative and semi-quantitative determination of aromatic hydrocarbons. Within this chemical family the method is used for the analysis of mononuclear (at a wavelength of 195 nm), dinuclear (at 225 nm) and trinuclear (at 255 nm) aromatic hydrocarbons.

Ultraviolet (UV) spectroscopy is also used as a detector in high-performance liquid chromatography (HPLC) for monitoring the column effluent, measuring the solute concentration, and to supplement elution volume data for identification purposes.

X-Ray Fluorescence Spectrometry

After an initial classifying IR spectrum is obtained on an unknown lubricant, usually a restricted elemental analysis is obtained. X-ray fluorescence spectrometry (XRF) is a convenient, fast and nondestructive method capable of simultaneously detecting and quantitating elements from sodium (atomic number 11) up in the periodic system. Both metals and nonmetals (such as P and S) in lubricant additives, and wear metals in the case of used oils, are easily detected and measured without regard to the chemical form in which the elements are present. The minimum amount of element that XRF can measure depends upon the element in question, but is usually in the parts-per-million (ppm) range. A complete qualitative analysis of a lubricant may take as little as two minutes. Since XRF analysis may take a sample in the form of a solid,

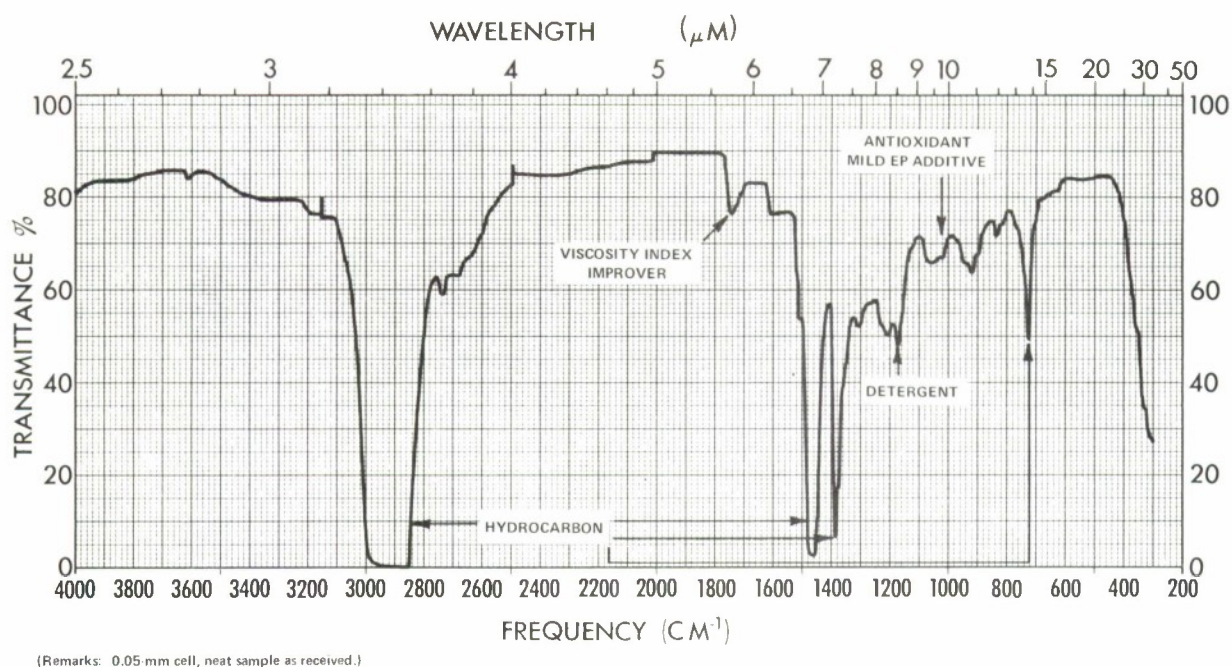


FIGURE 2. INFRARED SPECTRUM OF AL-5849

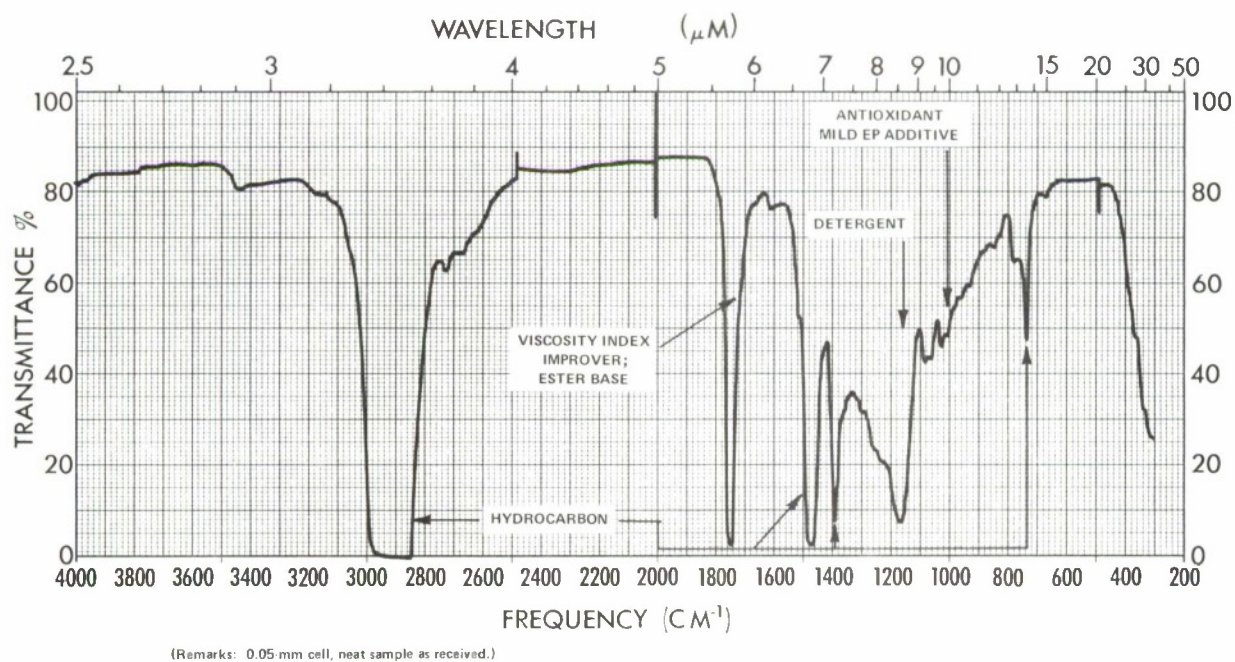


FIGURE 3. INFRARED SPECTRUM OF AL-5851

liquid, or powder, sediments in used oils may be analyzed on a homogenized sample or as a simple filtrate.

Results of the X-ray analysis may be used to direct further investigation toward restricted areas, i.e., toward the analysis of specific additives or may be used as a completed answer when only wear or contaminant metals identification is desired.

As is the case for most spectroscopic analytical methods, XRF is also capable of "fingerprinting" products. If the "fingerprint" of two products are not identical, the products are not identical. Atomic absorption techniques also continue to be used to supplement X-ray to provide quantitative data for certain metals.

The following several steps in the sequence of analysis simplify the complex lubricant mixture into components that are characterizable by existing analytical methods.

High-Performance Liquid Chromatography (HPLC)

Gel Permeation Chromatography (GPC)

This analytical method provides information about the sample's molecular size distribution (molecular weight range) without regard to chemical functionality. The following notes should be made:

- Larger molecules elute from the column before the smaller ones.
- Elution volume is inversely proportional to the effective molecular size of the sample in the solvent used.
- Peak sizes are not directly indicative of the amount of material represented by that peak, as the detector only measures the refractive index difference between the sample and the solvent. It follows, therefore, that if a sample's refractive index is widely different from that of the solvent, a relatively small amount of sample will give as large--or larger--peak than another component, whose refractive index is closer to that of the solvent.
- Peaks may deflect either positive or negative depending upon the sign of refractive index difference between the sample and the solvent.
- Since steric molecular geometry influences the molecular size to molecular weight relationship, true molecular weights are obtained through GPC only if the calibration curves prepared use the same series of compounds as those of the samples. While there are some experimental conversion factors available to correlate the molecular size (molecular weight) among several polymers, these "Q" factors are not normally used in this work, as these approximations should only be applied for the determination of the molecular weight range of a "single" known polymer composition. In the case of complex lubricating oil, one is restricted in the interpretation of the GPC

chromatograms to expressing molecular weight as "equivalent molecular weight" to the compound series used in the calibration curve preparation. At this facility *normal*-paraffins are used to MW = 560 and polystyrene standards up to MW = 3.7×10^6 to provide calibration curves over the appropriate molecular weight ranges as are indicated by Figures 4 and 5. These calibration curves are obtained under the appropriate optimized conditions for each molecular weight range.

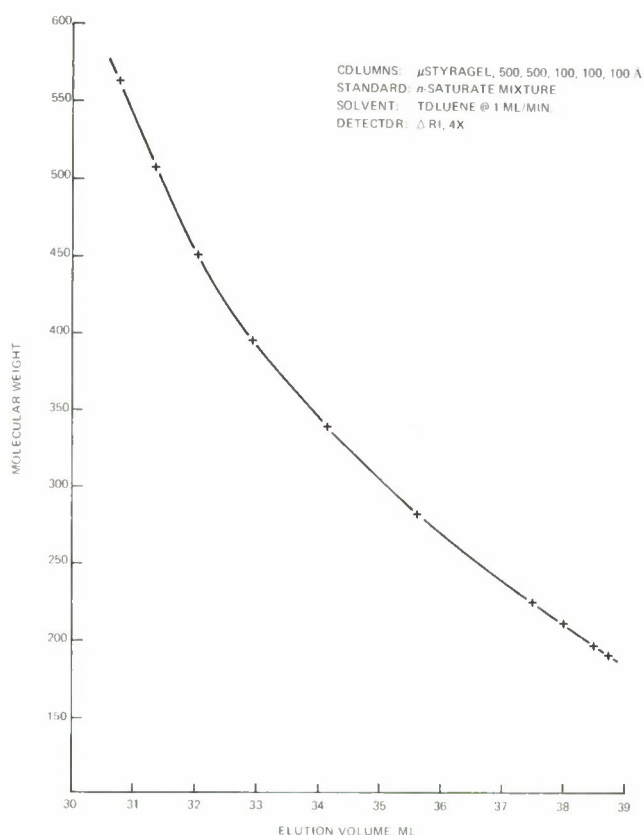


FIGURE 4. GEL PERMEATION CHROMATOGRAPHY CALIBRATION CURVE: LOW MOLECULAR WEIGHT RANGE

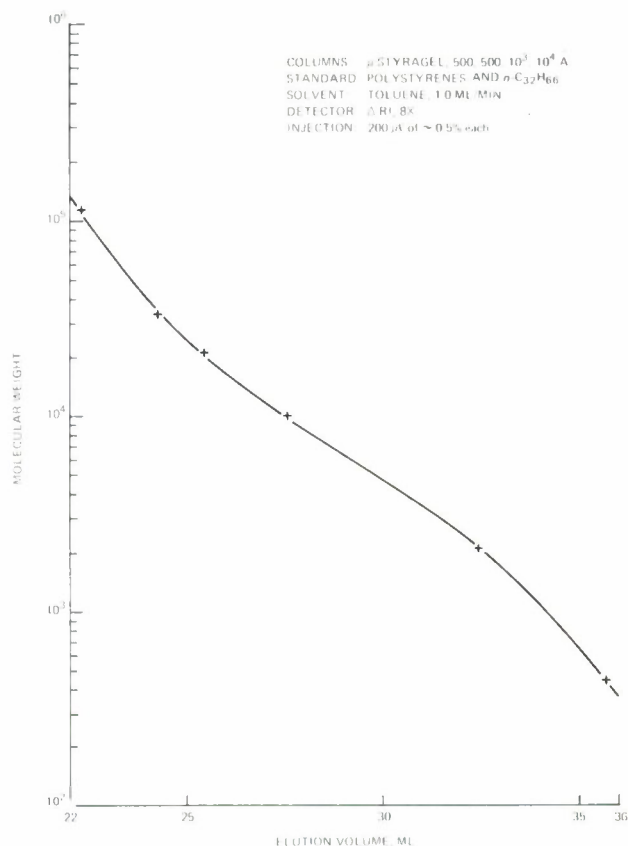


FIGURE 5. GEL PERMEATION CHROMATOGRAPHY CALIBRATION CURVE: HIGH MOLECULAR WEIGHT RANGE

A sample GPC chromatogram of a synthetic lubricant (AL-5724) is given in Figure 6A. This sample was run under conditions optimized for the high molecular weight (MW) range curve in Figure 5. For each peak the corresponding "equivalent molecular weight" (EMW) is indicated in Figure 6, viz., 85,000 for the high molecular weight peak and <400 for the low molecular weight peak. A series of diester based lubricants has been analyzed under conditions optimized for the low molecular weight range curve in Figure 4 giving the following results for the major base stock component:

Lubricant Code No.	GPC		Calculated MW
	EMW	1.37 EMW	
AL-5724	366	501	510
AL-F-1	362	496	500
AL-5075	344	471	468
AL-5096	316	433	426

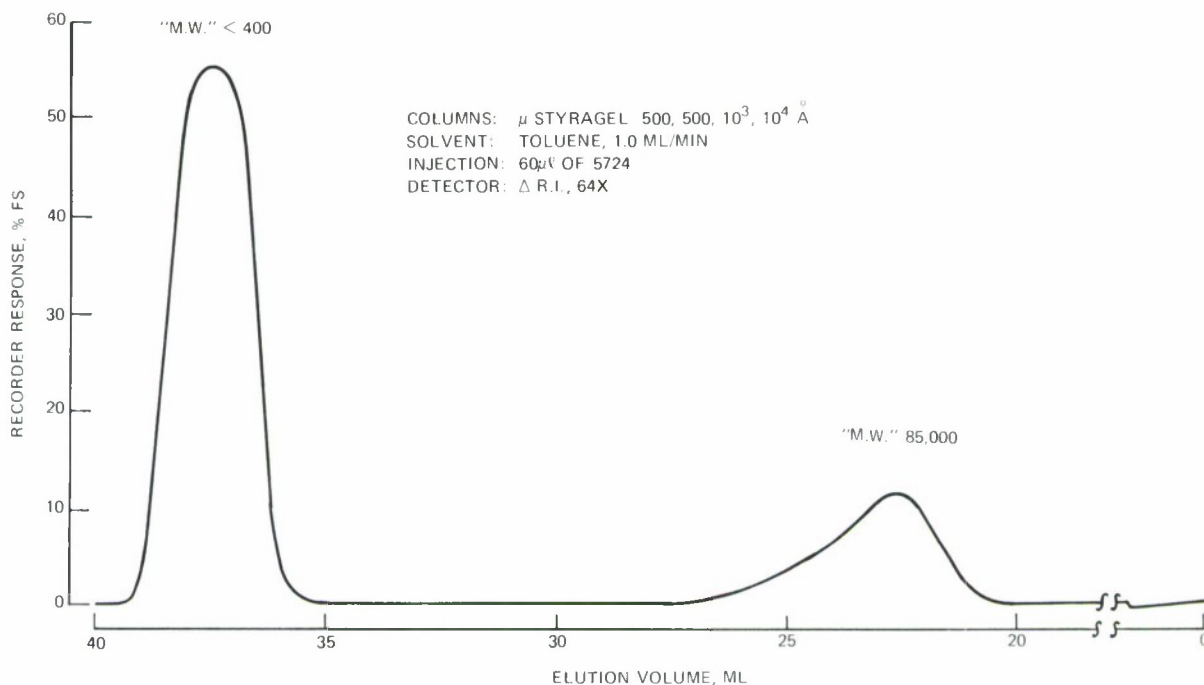


FIGURE 6A. GPC CHROMATOGRAM OF SYNTHETIC LUBRICANT AL-5724

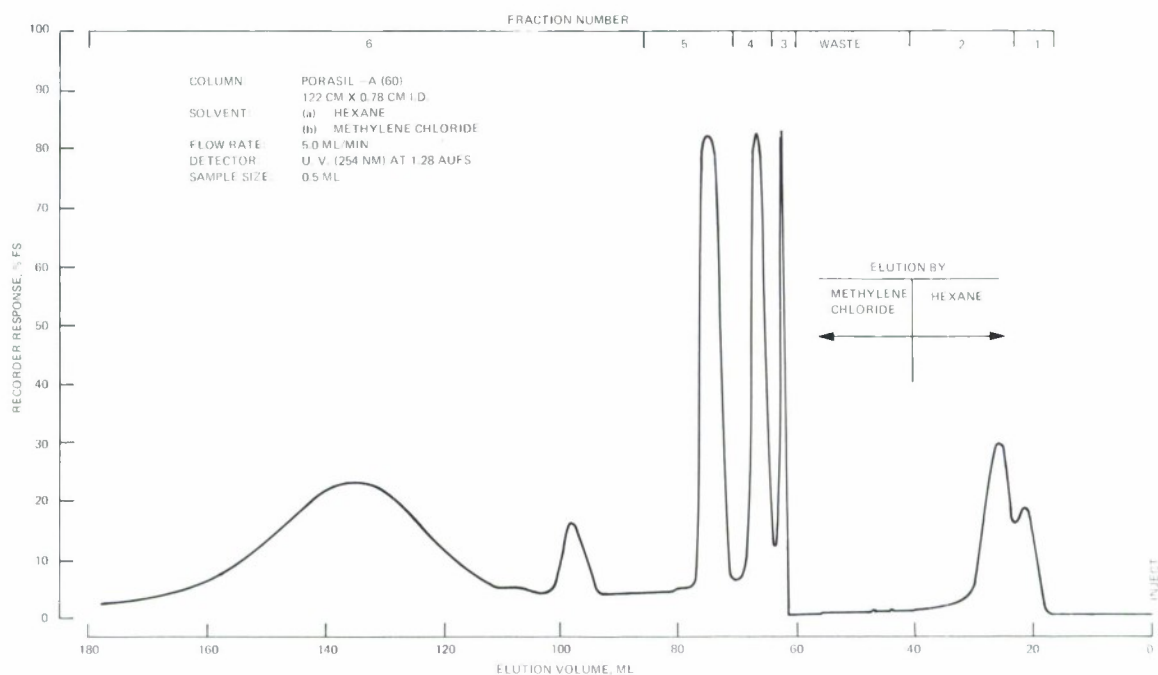


FIGURE 6B. HPLC CHROMATOGRAM OF AL-5594 OVER SILICA GEL

Since in this work the diester base-stock fraction of the finished lubricants were separated and their chemical composition determined, (as discussed later) these diesters were used to prepare a GPC calibration curve. This calibration curve now allows one to determine the molecular weight (instead of the "equivalent molecular weight") of similar species by GPC. The correlation coefficient between the *normal*-paraffin and polystyrene calibration curve and that prepared by the use of the separated diesters is 1.37; i.e., molecular weight of the diester is the equivalent molecular weight times 1.37, or

$$\text{M.W.} = 1.37 \text{ EMW.}$$

Preparative scale GPC separation of lubricants will yield a fraction with all the high molecular weight additives, (such as viscosity index improvers) and a low molecular weight fraction with the bulk of the sample, that contains--in the example cited--a diester based lubricant base-stock and possibly some other additives, that the original lubricant may have contained. These two fractions collected are handled separately.

The main emphasis rests on the identification of the base-stock material. In the examples cited, the base-stock is an ester type compound, as confirmed by IR spectroscopy. To understand the chemical make-up of the ester, this fraction has to be hydrolyzed to its building blocks: the alcoholic and the acidic components. Since, however, it is expected that the ester base-stock will contain some additives with molecular weights overlapping with that of the ester mixture, these additives should be removed from the main fraction prior to hydrolysis. This separation may be accomplished by adsorption-type liquid-solid chromatography, in a high-performance liquid chromatographic system.

Adsorption Chromatography

In adsorption chromatography (AC) the sample is dissolved in the lowest polarity solvent that it is soluble in, and the solution is then transferred onto a polar adsorbent. The sample will adsorb on the column. The eluting solvent will cause a differential migration process where the sample components are selectively retarded by the stationary phase (the adsorbent), the rate of which depends upon the polarity of the sample-adsorbent-eluting solvent system. The least polar compounds elute from the column first, the most polar ones last.

As was discussed earlier, GPC separates the components of a mixture according to molecular size, irrespective of the polarity (functionality) of the compounds present. If, therefore, a narrow molecular weight fraction of a GPC run is chromatographed over silica gel, the components will now be separated according to their polarity. If, for example, a high molecular weight fraction of a lubricant contained both a polyisobutylene type non-polar and a methacrylate type polar additives, this system will separate these two classes of polymers from each other. Similar separations will afford polar, non-polar and--if present--intermediate polarity compounds from other molecular weight ranges as well. By the combination of GPC and adsorption type HPLC, the originally highly complex lubricant mixture would now be separated into narrow molecular weight polar, non-polar and intermediate polarity

substances of such simplicity that they would be examinable by other instrumental techniques. The progress of these separation steps is followed by a differential refractometer, ultraviolet and infrared spectrophotometers, and--if needed--other instrumental techniques.

Monitoring the chromatographic effluent by an ultraviolet spectrophotometer is usually done at the fixed wavelength of 254 nm, where most of the UV absorbing compounds have an absorption line. On more modern instruments the sensitivity may be increased by monitoring at a different wavelength where the analyzed compound(s) have their highest molecular extinction coefficients, i.e., where the specific compound has the highest UV peak. (A small amount of material will then yield a relatively large peak.)

Ultraviolet spectra are also used for identification purposes in HPLC to supplement elution volume data. If, for example, a mixture of model (known) compounds is chromatographed, specific elution volumes are assigned to the individual species of the mixture. The elution volumes of the unknown mixture are then compared to those of known compounds. Coinciding elution volumes only *suggest* the identity of the species in question. Almost invariably the identity should be doublechecked by an independent method, such as UV scanning of the appropriate fraction. If the unknown mixture has a component whose elution volume and UV spectrum are identical, it may be said that the specific compound's presence is proven.

As an example, the analysis of a fully formulated lubricant (AL-5594), composed of a hybrid base stock illustrates the combined use of HPLC methods. GPC analysis showed this lubricant did not contain any high-molecular weight polymers (i.e., viscosity index improvers). Separation of this lubricant according to polarity by HPLC over a silica gel column (Porasil-A, 122 cm long by 0.78 cm I.D.) using step-gradient elution (hexane followed by methylene chloride) yielded the chromatogram in Figure 6B. Cut-points for the six fractions collected are indicated on the chromatogram together with the experimental conditions employed. Five successive injections were made, the appropriate fractions were combined and the solvents were stripped at room temperature using a rotary vacuum evaporator. Each of the recovered fractions were weighed to establish quantitative recovery from the column. The following results were obtained:

<u>Fraction No.</u>	<u>% (wt) of Lubricant</u>	<u>Notes</u>
1	66.8	Hydrocarbon, clear liquid
2	.5	Clear liquid
3	1.0	Crystalline substance
4	1.4	Yellow liquid
5	3.3	Yellow liquid
6	27.0	Ester, yellow liquid

Fractions 2 through 5 have not yet been identified, but it is suspected that these are additives. (Identification of additives will be the subject of future studies.) Fractions 1 and 6 are the major base stock components. These fractions are identified in a later section of this report as: fraction 1, synthetic hydrocarbon, oligimer of decene-1; fraction 6, ester, 2-ethylhexylazelate.

If it appears that a narrow molecular weight, narrow polarity fraction still contains several components, these fractions may be separated by a "reversed-phase" HPLC technique.

Reversed-Phase HPLC

In reversed-phase chromatography, compounds within a narrow polarity range may be separated using--usually--a non-polar adsorbent and elution is accomplished by polar solvent(s). Optimal separation in this operation usually involves the use of a "gradient elution" system, where the polarity of the solvent is changed at a predetermined manner. Such a system is capable of separating, for example, highly polar additives from each other, such as the barium sulfonates and zinc dialkyl (or diaryl) dithiophosphates⁽¹⁹⁾.

Several samples of diester based finished lubricants were separated at this facility to produce essentially additive-free diester base-stock. In order to determine the chemical make-up of the diesters, they were hydrolyzed into the components from which they were manufactured, namely, the alcohol(s) and dibasic acid(s), which, in turn, were identified and quantitatively measured by GC as discussed in a latter section.

Chemical Hydrolysis of Diesters

Hydrolysis of an acid ester may be accomplished in a number of ways. Alcoholic potassium hydroxide in water after about a two-hour reflux yields the potassium salt of the ester's carboxylic acid together with the alcoholic fraction. These constituents are separated using classical chemical work-up procedures. The alcoholic component is extracted by diethyl ether from the basic reaction mixture, after which the carboxylic acid salt is acidified by a mineral acid (HCl), and the carboxylic acid component is then extracted. The alcoholic and acidic components are then derivatized and analyzed by gas chromatography. The method for derivatization is discussed in Appendix A.

Gas Chromatography

In the overall purpose of this program it was desired to characterize lubricants both qualitatively and quantitatively, for which gas chromatography (GC) offers the greatest single instrumental-analytical capability. The general gas chromatographic approach taken was to use a method which recovered as accurately as was reasonable all of the sample (whether neat or pre-treated lubricant) and to use as high an analytical recovery temperature as feasible. For this reason, a method essentially equivalent to ASTM D2887 (Test for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography)⁽²⁰⁾ with a resolution of approximately 5.0 was used for both the lubricants and any derivatized lubri-

cant hydrolysis products. Two such gas chromatography methods have been developed for evaluating high boiling hydrocarbons that are detailed in Appendix B.

Boiling point distribution of mineral oils can be done both by molecular distillation and gas chromatography. The volatility characteristics of four lubricants as determined by molecular distillation are shown in Figure 7. Two of these oils are mineral oils and the other two are synthetic lubricants. These same oils were evaluated by GC and the resulting boiling point distributions are shown in Figure 8. GC not only has higher resolution, but can be more accurate and less time-consuming than the molecular distillation approach. The GC approach assumes that the hydrogen flame ionization detector has essentially equal response for all hydrocarbons in the lubricant samples. Molecular distillation was used to give a residue portion (approximately 1050°F and greater) and a distillate portion for verification of quantitative GC analysis. This distillate by GC analysis showed essentially no residue based on a C₉-C₁₁ internal standard and confirmed the assumption of equal detector response for the hydrocarbons present. The gas chromatographic detector output recordings are computer reduced to form boiling point distribution data such as in Figure 8.

Figure 9 gives a visual display of chromatograms for the Altamont crude oil standard and several mineral oil based lubricants. The Altamont crude oil is a high *n*-saturate material obtained from the Bureau of Mines, Bartlesville, Oklahoma. The lubricants in descending order are: an SAE 30 reference engine oil (REO 203), a higher viscosity mineral oil (AL-5850), and a "synthetic" lubricant (AL-5851) which appears to and did contain some mineral oil based on the broad hump character of the chromatogram and some synthetic ester material (verified by IR in Figure 3) based on the three significantly sharp peaks in the chromatogram. As is apparent from the chromatogram and is quantitated in Table 2 based on the internal standard, the samples contain material boiling above the end of the analysis time (and remain in the column). Any high molecular weight viscosity index improver will also stay in the column and is accounted for as a "residue" in the analytical procedure.

When interest in the analysis of MIL-H-6083 and MIL-H-46170 hydraulic oils and APG PD-1 arctic oils led to their submission to GC boiling point analysis, the same procedure currently in use for mineral oils was used to provide evaluations. The chromatograms in Figure 10 are good examples. In descending order, the first two lubricant chromatograms are of synthetic hydraulic oils formulated to the same specification but made by two different suppliers. The GC chromatograms and data amplified differences between the two lubricants' compositions as well as the major base stock similarity. The third chromatogram vividly demonstrates the very high volatility of this lubricant (AL-5074), composed primarily of a kerosene base stock, compared to the upper two synthetic based fire resistant lubricants, all three of which are "hydraulic fluids". The boiling point distribution data for AL-5074 gave a residue value of 15% wt, most of which would be expected to be viscosity index improver.

Based on qualitative GC analysis of representative synthetic lubricants on Dexsil 300, OV-17, and SE-30 coated columns, a boiling point distri-

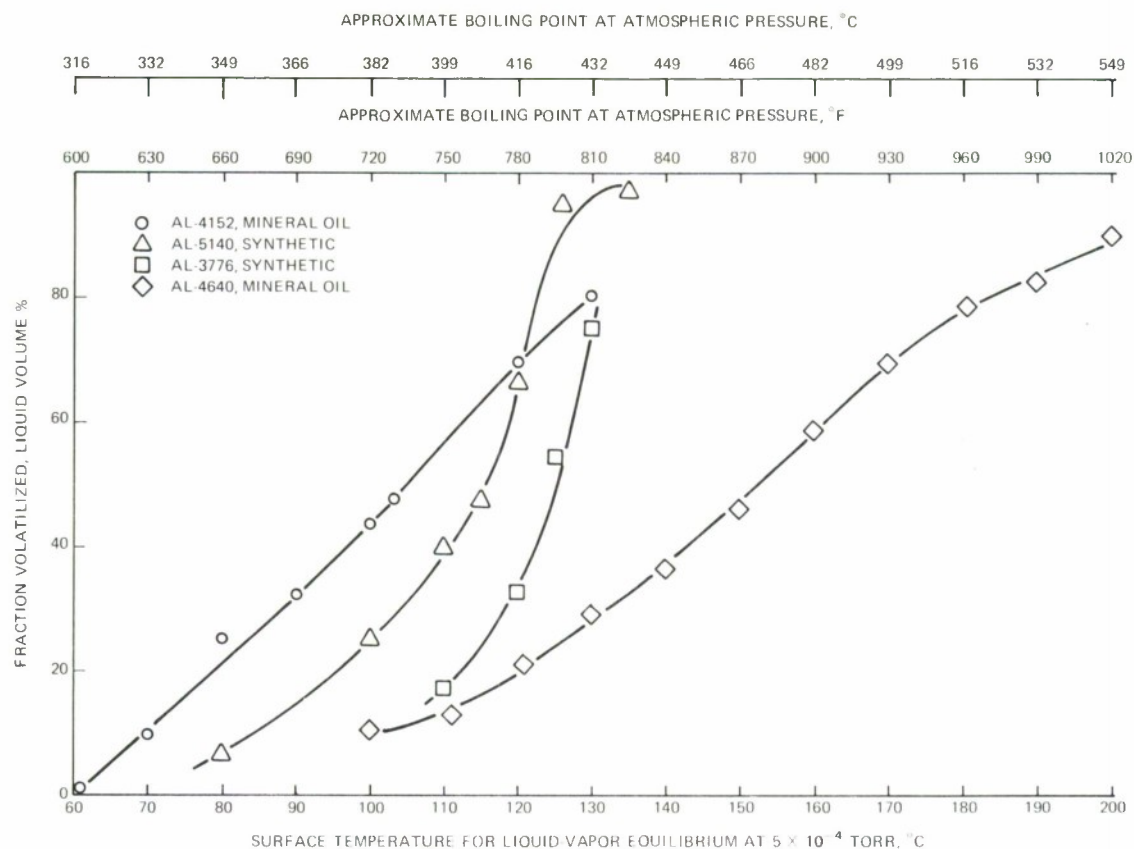


FIGURE 7. VOLATILITY CHARACTERISTICS OF LUBRICANTS AS DETERMINED BY MOLECULAR DISTILLATION

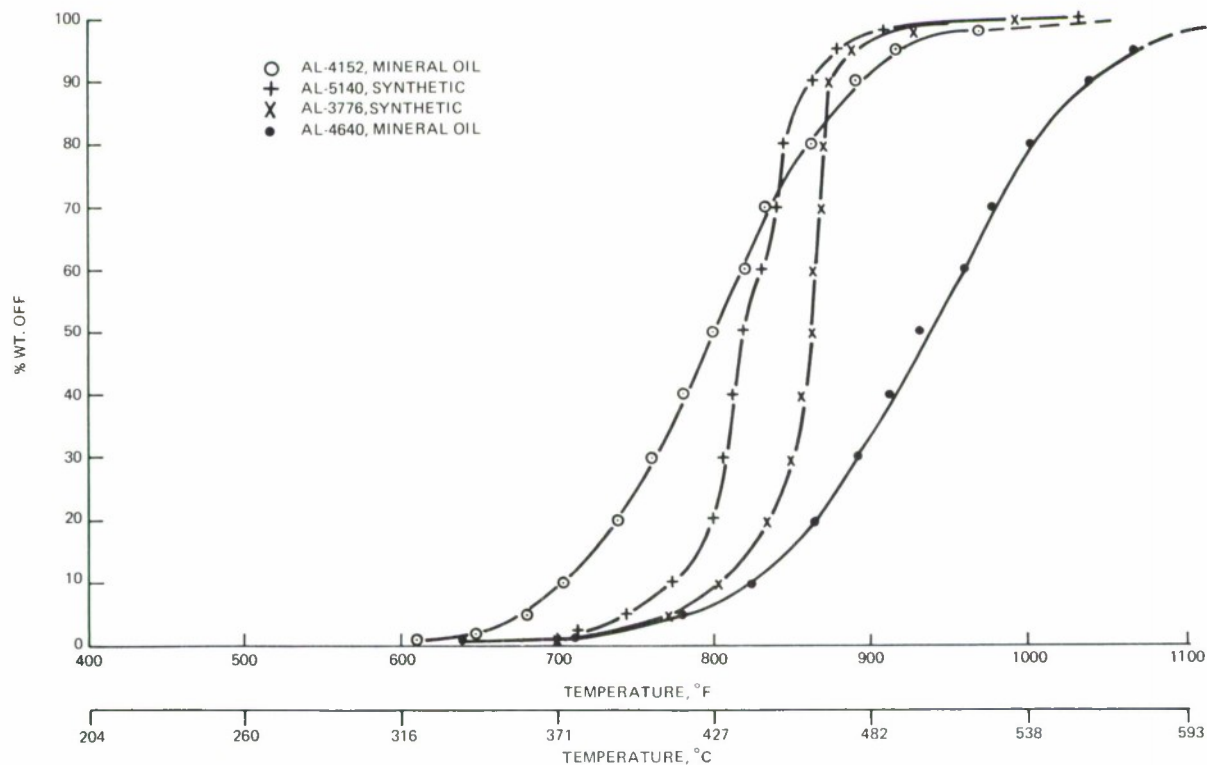


FIGURE 8. BOILING POINT DISTRIBUTION OF LUBRICANTS BY GAS CHROMATOGRAPHY
 (Mineral Oil Method, C_9 - C_{11} Internal Standards)

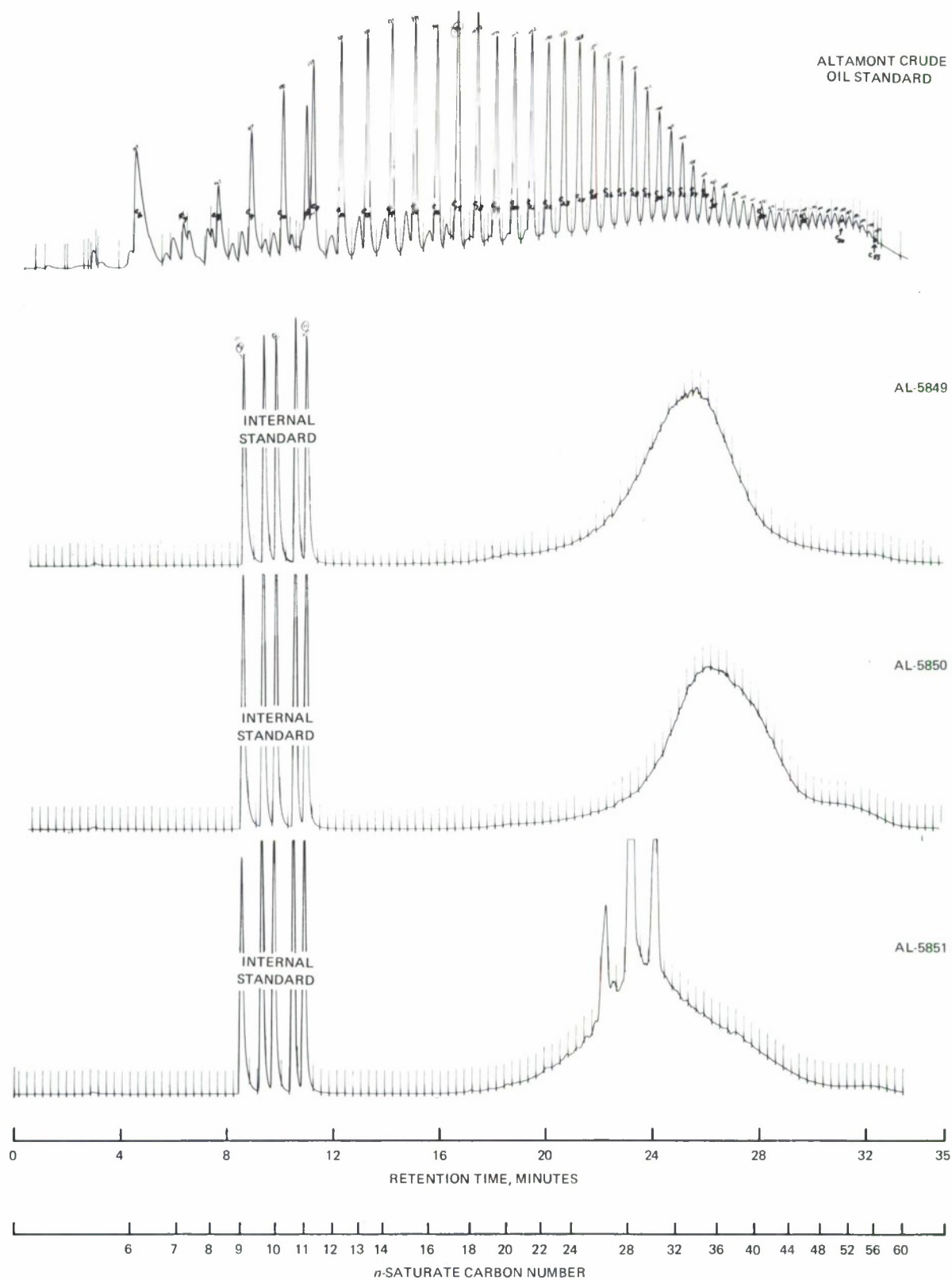


FIGURE 9. GAS CHROMATOGRAMS FOR ALTAMONT CRUDE OIL AND THREE LUBRICANTS

TABLE 2. BOILING POINT DISTRIBUTION BY GAS CHROMATOGRAPHY
(Mineral Oil Procedure Using C₉-C₁₁ Internal Standard)

AL-5849				AL-5851				AL-5850			
Percent Off	Deg.C	Percent Off	Deg.C	Percent Off	Deg.C	Percent Off	Deg.C	Percent Off	Deg.C	Percent Off	Deg.C
0.5	291	48.0	477	0.5	313	46.0	453	0.5	316	46.0	496
1.0	326	49.0	477	1.0	336	47.0	453	1.0	351	47.0	501
2.0	349	50.0	477	2.0	360	48.0	453	2.0	381	48.0	501
3.0	367	51.0	477	3.0	372	49.0	453	3.0	398	49.0	501
4.0	379	52.0	483	4.0	377	50.0	453	4.0	410	50.0	501
5.0	391	53.0	483	5.0	383	51.0	453	5.0	416	51.0	501
6.0	396	54.0	483	6.0	389	52.0	458	6.0	427	52.0	507
7.0	402	55.0	483	7.0	395	53.0	458	7.0	433	53.0	507
8.0	408	56.0	483	8.0	401	54.0	458	8.0	439	54.0	507
9.0	414	57.0	483	9.0	401	55.0	458	9.0	444	55.0	507
10.0	419	58.0	488	10.0	407	56.0	458	10.0	444	56.0	507
11.0	419	59.0	488	11.0	412	57.0	464	11.0	451	57.0	512
12.0	426	60.0	488	12.0	412	58.0	464	12.0	451	58.0	512
13.0	426	61.0	488	13.0	412	59.0	464	13.0	456	59.0	512
14.0	431	62.0	488	14.0	418	60.0	470	14.0	456	60.0	512
15.0	431	63.0	488	15.0	418	61.0	470	15.0	462	61.0	512
16.0	437	64.0	494	16.0	418	62.0	470	16.0	462	62.0	518
17.0	437	65.0	494	17.0	418	63.0	476	17.0	462	63.0	518
18.0	437	66.0	494	18.0	418	64.0	476	18.0	467	64.0	518
19.0	443	67.0	494	19.0	424	65.0	476	19.0	467	65.0	518
20.0	443	68.0	494	20.0	424	66.0	481	20.0	467	66.0	523
21.0	443	69.0	499	21.0	424	67.0	481	21.0	467	67.0	523
22.0	448	70.0	499	22.0	430	68.0	481	22.0	473	68.0	523
23.0	448	71.0	499	23.0	430	69.0	487	23.0	473	69.0	523
24.0	448	72.0	499	24.0	430	70.0	487	24.0	473	70.0	529
25.0	448	73.0	499	25.0	430	71.0	487	25.0	473	71.0	529
26.0	454	74.0	505	26.0	436	72.0	493	26.0	479	72.0	529
27.0	454	75.0	505	27.0	436	73.0	493	27.0	479	73.0	529
28.0	454	76.0	505	28.0	436	74.0	498	28.0	479	74.0	534
29.0	454	77.0	505	29.0	436	75.0	498	29.0	479	75.0	534
30.0	460	78.0	511	30.0	436	76.0	504	30.0	479	76.0	534
31.0	460	79.0	511	31.0	436	77.0	504	31.0	484	77.0	539
32.0	460	80.0	511	32.0	436	78.0	509	32.0	484	78.0	539
33.0	460	81.0	516	33.0	436	79.0	509	33.0	484	79.0	545
34.0	460	82.0	516	34.0	441	80.0	515	34.0	484	80.0	545
35.0	466	83.0	516	35.0	441	81.0	515	35.0	484	81.0	550
36.0	466	84.0	516	36.0	441	82.0	520	36.0	490	82.0	556
37.0	466	85.0	527	37.0	441	83.0	520	37.0	490	83.0	556
38.0	466	86.0	527	38.0	441	84.0	526	38.0	490	84.0	561
39.0	466	87.0	532	39.0	441	85.0	531	39.0	490	85.0	566
40.0	471	88.0	538	40.0	441	86.0	537	40.0	490	86.0	576
41.0	471	89.0	543	41.0	447	87.0	542	41.0	496	87.0	581
42.0	471	90.0	548	42.0	447	88.0	547	42.0	496	88.0	586
43.0	471	91.0	559	43.0	447	89.0	553	43.0	496	89.0	591
44.0	471	92.0	564	44.0	447	90.0	568	44.0	496	90.0	601
45.0	471	93.0	579	45.0	453			45.0	496		
46.0	477	94.0	589								
47.0	477	95.0	609								
Residue = 4.5%				Residue = 8.1%				Residue = 9.4%			

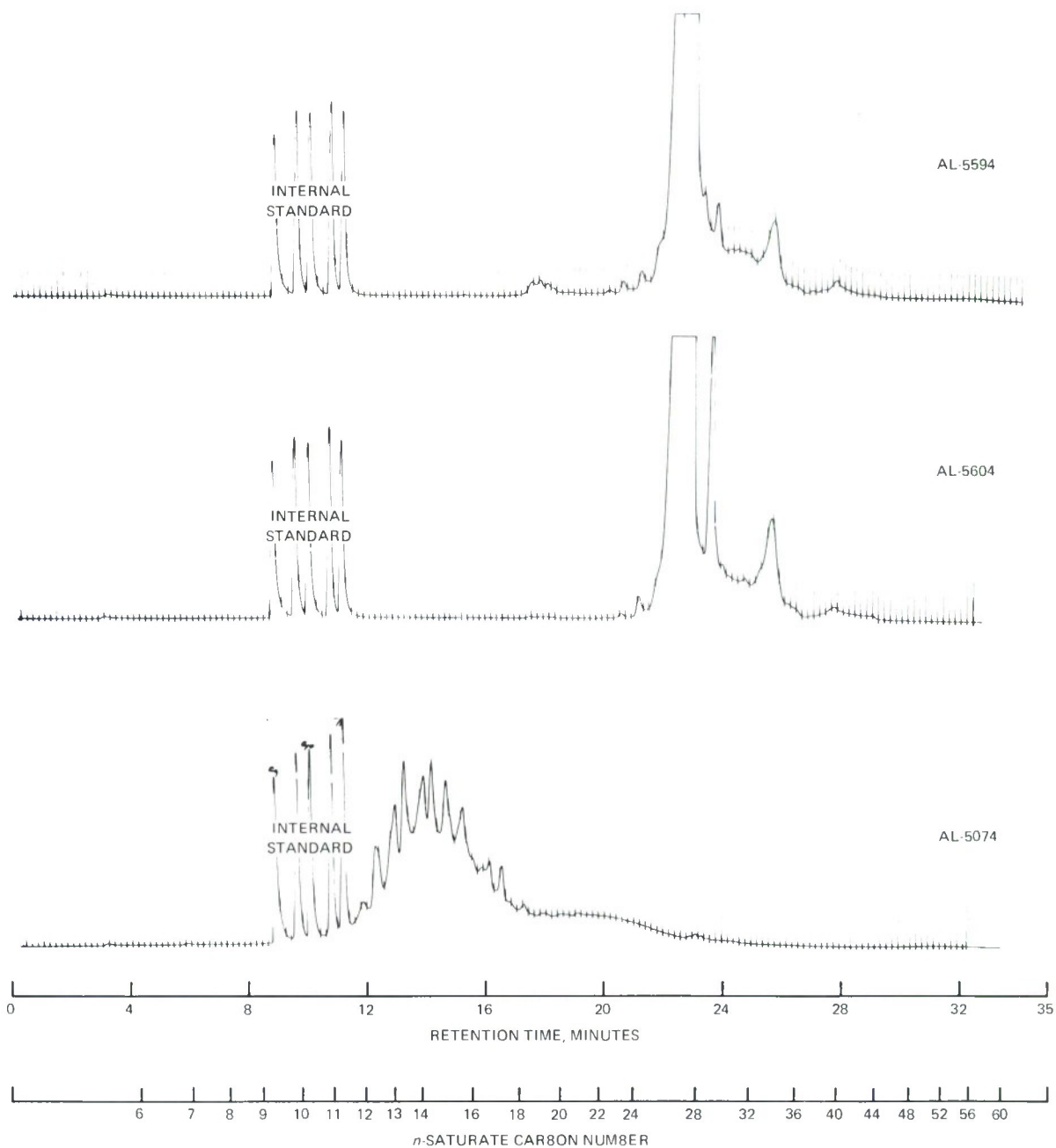


FIGURE 10. BOILING POINT DISTRIBUTION OF THREE HYDRAULIC LUBRICANTS
(Mineral Oil Procedure with C_9 - C_{11} Internal Standard)

bution technique which was essentially ASTM D2887 with the addition of an internal standard and dilution with carbon disulfide was selected. Routine data reduction was also simplified by treating this solution as a straight ASTM D2887 analysis. The laboratory data system is calibrated for boiling points using a *n*-saturated hydrocarbon standard (Appendix A), the chromatogram of which is shown in Figure 11. Three chromatograms of di-ester based lubricants are also shown in Figure 11. The first two (AL-3776 and AL-5075) are of the same lubricant obtained at two different points in time and are chromatographically identical. (Note: The first chromatogram is at a higher recorder attenuation than the second one and therefore appears to be slightly different. This is due to the electrometer amplification setting which can be visually eliminated by comparing the peak intensity of the internal standard.) The third chromatogram (AL-5096) is of a synthetic lubricant having some high boiling (>539°C) ester base stock composed of C₁₃ and higher alcohols and C₁₁ and higher di-acids.

Synthetic oils whether they be arctic, polymer thickened, or hydraulic oils, are generally approached in the same way for GC analysis. It is assumed that at least some part of the oil (additives or high boiling base stock) will either not respond as strongly to the hydrogen flame ionization detector (HFID) as the *n*-saturate standards or hydrocarbons in general and will result in a residue in the boiling point distribution method. Additionally, these materials may show GC residues simply because some of the oil components remain in the column due to their low volatility (high boiling point). Ester type base stock contains oxygen-carbon bonds which can also reduce HFID response. For example, the relative sensitivity of isoamylacetate is reported to be 0.62 compared to 1.00 for heptane⁽²¹⁾. In order to evaluate the synthetic lubricant diester response (relative sensitivity), four base stocks were evaluated by boiling point distribution using the simplified C₉-C₁₁ hydrocarbon internal standard method. These base stocks and their calculated relative sensitivity were as follows:

<u>Base Stock</u>	<u>Relative Sensitivity</u>
Di-2-ethylhexyl azelate	0.96
Di-iso-octyl azelate	0.96
Isodecyl adipate	1.03
Tridecyl adipate	0.99

Since these values are so close to unity no correction factors need be introduced when using the boiling point distribution method. Residue values, when reported, are assumed to be, in part, low response additives and materials (base stock or additive) boiling above 539°C (1000°F). Hence, using the data system output (Table 3) for the three lubricants in Figure 11, residue values and boiling point distribution temperatures can be tabulated as in Table 3. An example of the calculation approach is also given in Table 3.

While any two given synthetic based lubricants may appear to be very similar or even identical based on boiling point distribution, hydrolysis of the ester can result in products which clearly differentiate between the lubricants. These acidic and alcoholic hydrolysis products

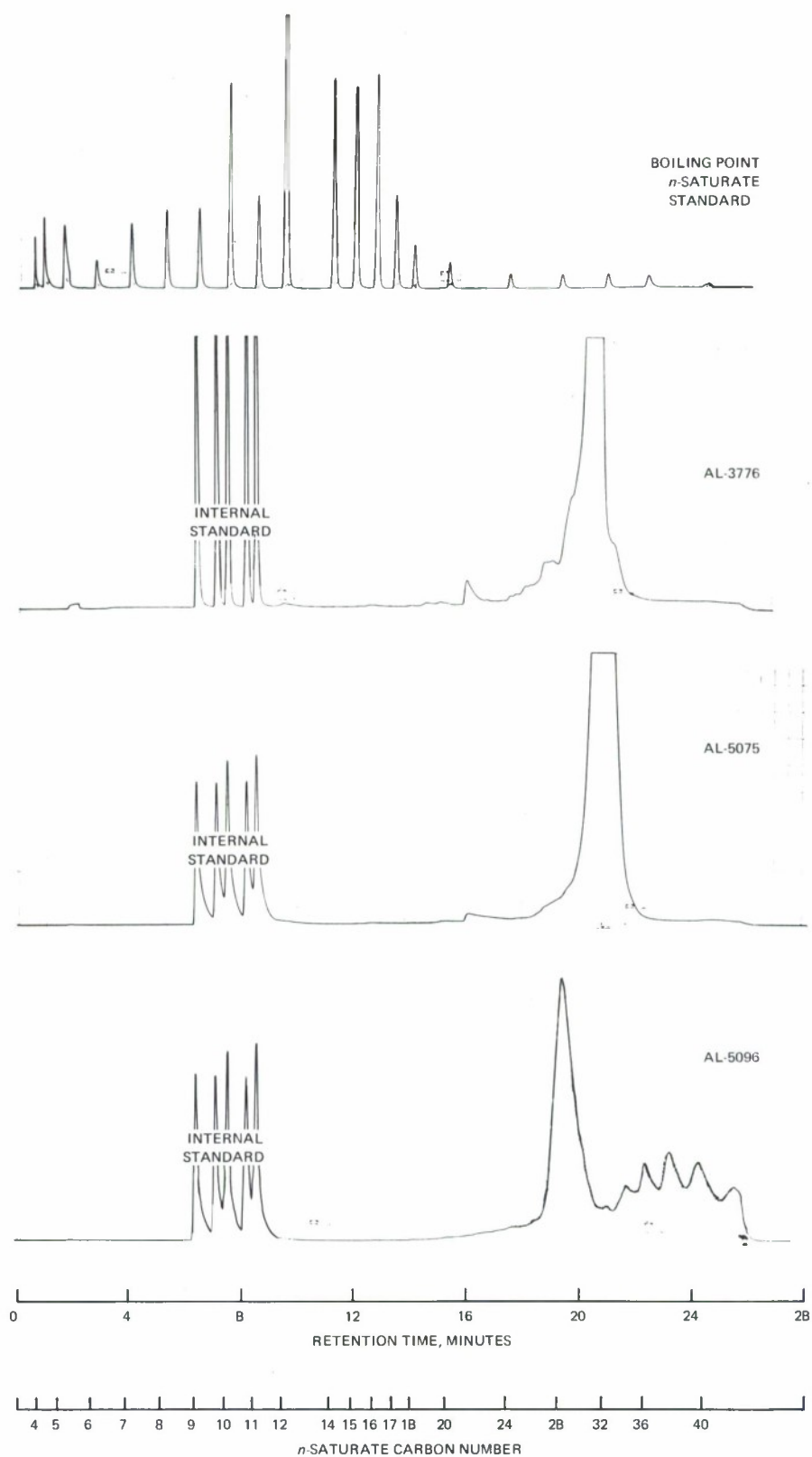


FIGURE 11. BOILING POINT DISTRIBUTION OF THREE SYNTHETIC LUBRICANTS
*(Synthetic Lubricant Method Using C_9 - C_{11} Internal Standard and
 Simplified Data Reduction Procedure)*

TABLE 3. BOILING POINT DISTRIBUTION OF SYNTHETIC LUBRICANTS
(Simplified C₉-C₁₁ Internal Standard Method for Synthetic Lubricants)*
(Note: *Italicized* calculated values are used in Table 4.)

AL-3776 [18.2% wt C ₉ -C ₁₁] 81.8% wt Sample				AL-5075 [17.7% wt C ₉ -C ₁₁] 82.3% wt Sample				AL-5096 [19.4% wt C ₉ -C ₁₁] 80.6% wt Sample								
Percent Off		Deg. C		Percent Off		Deg. C		Percent Off		Deg. C		Percent Off		Deg. C		
Internal Standard	IBP	148				IBP	148					IBP	147			
	1	150	51	460	1	150	51	462	1	148	51	439				
	2	152	52	461	2	152	52	462	2	151	52	440				
	3	155	53	461	3	155	53	462	3	153	53	441				
	4	160	54	461	4	162	54	463	4	155	54	442				
	5	165	40	55	462	5	165	40	55	463	5	163	55	443		
	6	166	56	462	6	167	56	463	6	165	56	444				
	7	168	57	462	7	169	57	464	7	166	40	57	445			
	8	171	58	462	8	172	58	464	8	168	58	447				
	9	173	59	463	9	174	59	465	9	171	59	448				
	10	175	60	463	10	175	60	465	10	173	60	450				
	11	176	61	463	11	177	61	465	11	174	61	452				
	12	179	62	464	12	181	62	465	12	175	62	455				
	13	186	50	63	464	13	187	50	63	466	13	176	63	458		
	14	188	64	465	14	189	64	466	14	180	64	462				
	15	190	65	465	15	191	65	466	15	186	50	65	467			
	16	192	66	465	16	194	66	466	16	187	66	472				
	17	195	67	465	17	196	67	467	17	190	67	477				
	18	196	68	466	18	197	68	467	18	192	68	481				
	19	197	69	466	19	198	69	467	19	194	69	484				
	20	198	70	466	20	201	70	467	20	195	70	487				
	21	201	71	466	21	209	60	71	468	21	196	71	491			
	22	219	60	72	467	22	343	72	468	22	197	72	493			
	23	352	73	467	23	371	73	468	23	199	60	73	496			
	24	372	74	467	24	396	74	469	24	201	74	498				
	25	393	75	467	25	417	75	469	25	209	75	501				
	26	408	76	468	5	26	426	76	470	26	347	76	503			
	5	27	418	77	468	27	433	77	470	27	374	77	507			
	28	424	78	468	28	438	78	470	28	389	78	510				
	29	429	79	469	29	442	70	79	471	29	401	79	512			
	30	434	70	80	469	10	30	446	80	471	30	410	80	514		
10	31	438	81	470	31	448	81	471	31	417	70	81	516			
32	441	82	470	32	451	82	472	32	422	82	518					
33	443	83	470	33	452	83	472	33	424	83	520					
34	446	84	471	34	453	84	472	10	34	425	84	522				
35	448	85	471	35	454	85	473	35	427	85	525					
36	450	86	471	36	455	86	473	36	428	86	528					
37	451	87	472	37	456	80	87	474	37	429	87	531				
38	452	80	88	472	20	38	456	88	475	38	430	88	533			
20	39	453	89	472	39	457	89	475	39	430	80	89	536			
40	455	90	473	40	457	90	476	40	431	81	90	538				
41	455	91	474	41	458	91	476	41	432	91	540					
42	456	92	475	42	458	92	477	20	42	432	92	543				
43	456	93	476	43	459	93	478	43	433	93	546					
44	457	94	476	44	460	94	480	44	434	94	549					
45	457	95	478	45	460	90	95	481	45	435	95	553				
46	458	90	96	480	30	46	460	96	483	46	435	96	557			
30	47	458	97	483	47	461	97	487	47	436	97	560				
48	459	98	492	48	461	98	498	48	437	98	563					
49	460	99	526	49	461	95	99	533	49	437	99	567				
50	460	95	FBP	539	50	461	96	FBP	539	30	50	438	94	FBP	569	
Residue = 100-[100(78/82)] Residue = 5% above 539°C Normalization factor = 95/77 = 1.23				Residue = 100-[100(79/82)] Residue = 4% above 539°C Normalization factor = 96/78 = 1.23				Residue = 100-[100(75/81)] Residue = 6% above 569°C Residue = 19% above 539°C Normalization factor = 94/74 = 1.27								

*Italicized numbers represent calculated percent off values for neat sample.

are analyzed by GC under the same conditions as the parent lubricant; however, derivatization and peak normalization techniques are used. Both OV-17 and SE-30 GC columns were initially used to evaluate the derivitization products. The more polar OV-17 tended to decrease the separation of the non-polar alcohol derivatives from the more polar derivitization solution, hence SE-30 columns are routinely used. Since some synthetic hydrocarbon base stocks, non-hydrolyzed base stock or non-hydrolyzable additives may be present, the same GC operating conditions for synthetic lubricants is used for derivatized alcoholic and acidic products as for synthetic lubricants. Figure 12 contains the chromatograms of alcoholic products from the three lubricants in Figure 11. The chromatogram indicates that hydrolysis was complete other than for the small peak (an additive perhaps) in the first two oils. Identification of the alcohols based on retention time can be accomplished by analysis of base stock alcohols used in the preparation of esters. A more sophisticated silylation approach, discussed in Appendix A, was chosen which would give sharper, better-defined peaks. In addition to the primary-alcohol standard, three alcohol base stocks were obtained and used to classify alcoholic products of diester base-stocks in this approach. Figure 13 compares in descending order the chromatograms of silylated iso-octyl alcohol, iso-decyl alcohol, iso-tridecyl alcohol, and the C₇ through C₁₀ primary alcohol standard which was spiked with 2-ethyl hexanol. Based on the silylated alcohol retention time data from Figure 13, the silylated alcohol peaks from lubricants of unknown composition can be evaluated.

The alcoholic products of the three lubricants in Figure 11 were silylated and their chromatograms are shown in Figure 14. The peak areas attributed to alcohols are normalized to 100% and reported in addition to the identified lubricant acids also obtained from hydrolysis. The acids from the three lubricants in Figure 11 were silylated and their chromatograms are shown in Figure 15. An acid standard containing C₅-C₁₀ dibasic acids was also silylated and the chromatogram included in Figure 15. Comparison of retention time for the acids provides identification. The peaks attributed to the acids are normalized to 100% wt and reported for each lubricant. Tabulated data reports for these three lubricants in addition to several others are given in Table 4. These data-reports (Table 4) are readily used to identify, characterize, and compare ester-based lubricants according to boiling point distribution and composition.

CONCLUSIONS

Data commonly used to describe lubricants do not provide the detailed compositional information generally needed to define base stock and additive character and identify the source of new and used lubricants. Analytical/instrumental methods are being developed and applied in a continuing effort to better characterize lubricants. In summary, this report has demonstrated the viability of presently used analytical methods in that:

1. An analytical approach proposing no new art but placing emphasis on the utilization of existing methods in a logical sequence as a guide to generate useful information about lubricant composition has been presented.

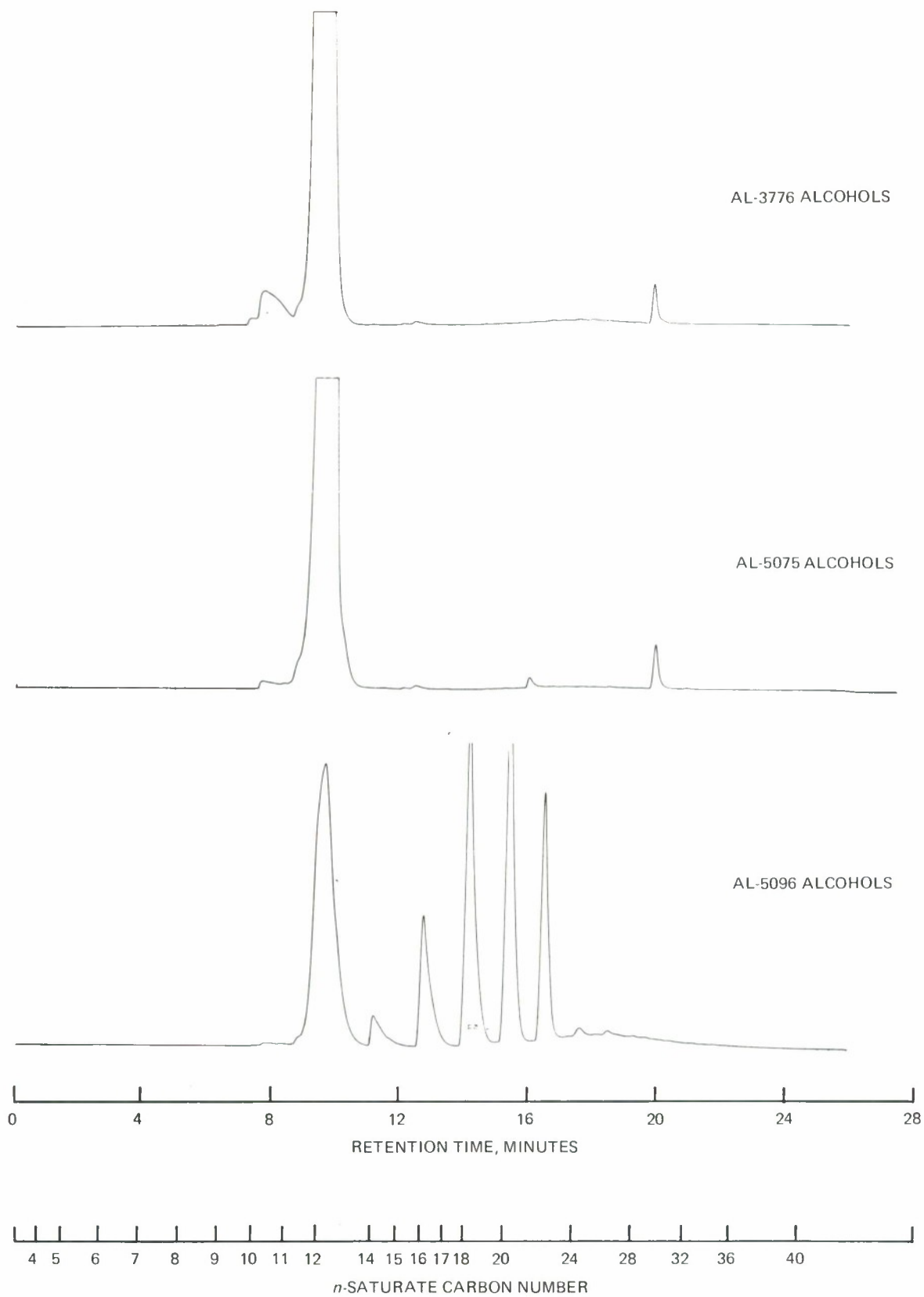


FIGURE 12. ALCOHOLIC PRODUCTS FROM HYDROLYSIS OF THREE DI-ESTER BASED LUBRICANTS
(Note: Same lubes as in Figure 11.)

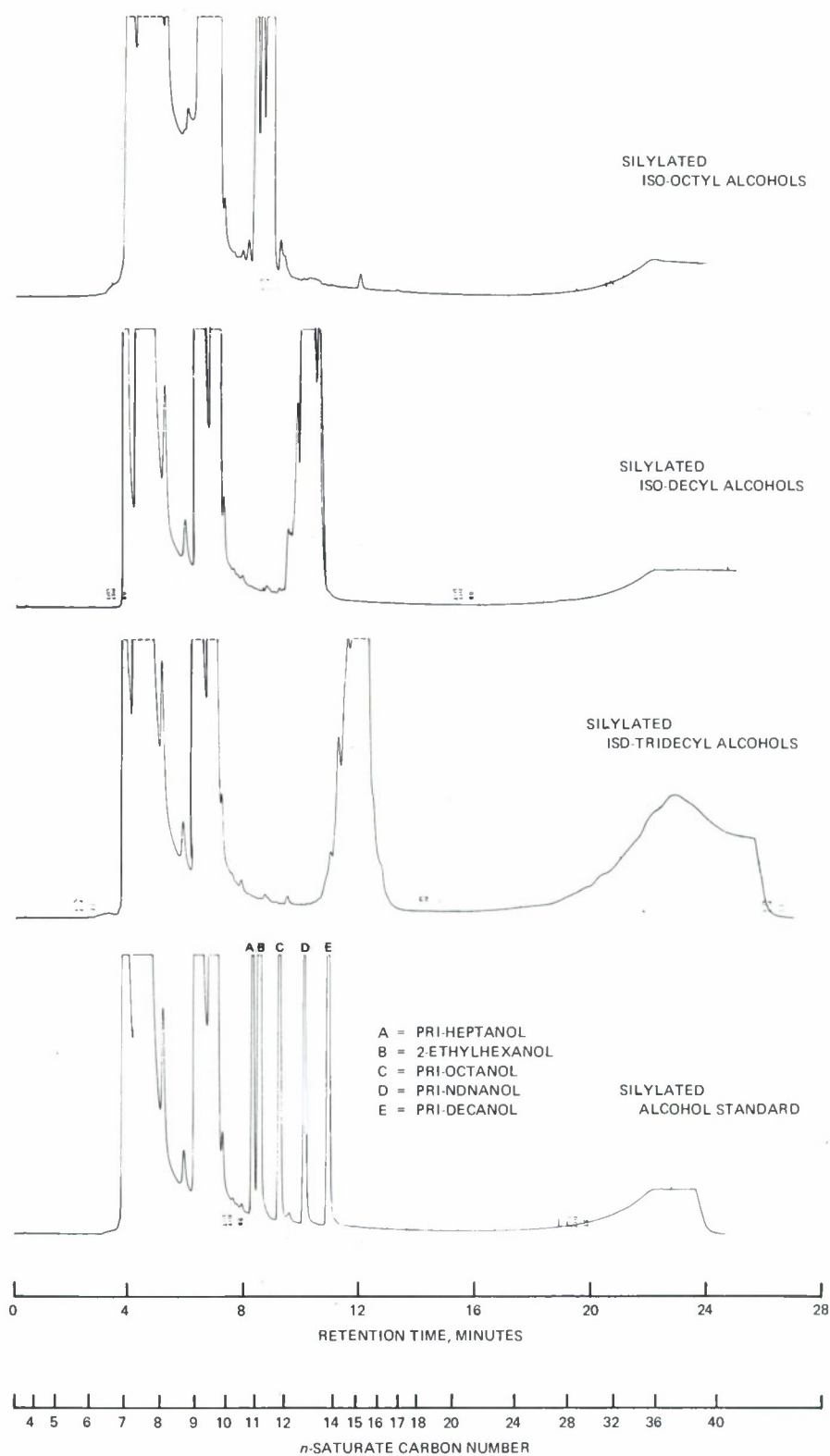


FIGURE 13. CHROMATOGRAMS OF SILYLATION PRODUCTS OF ALCOHOLS
FROM BLEND STOCKS

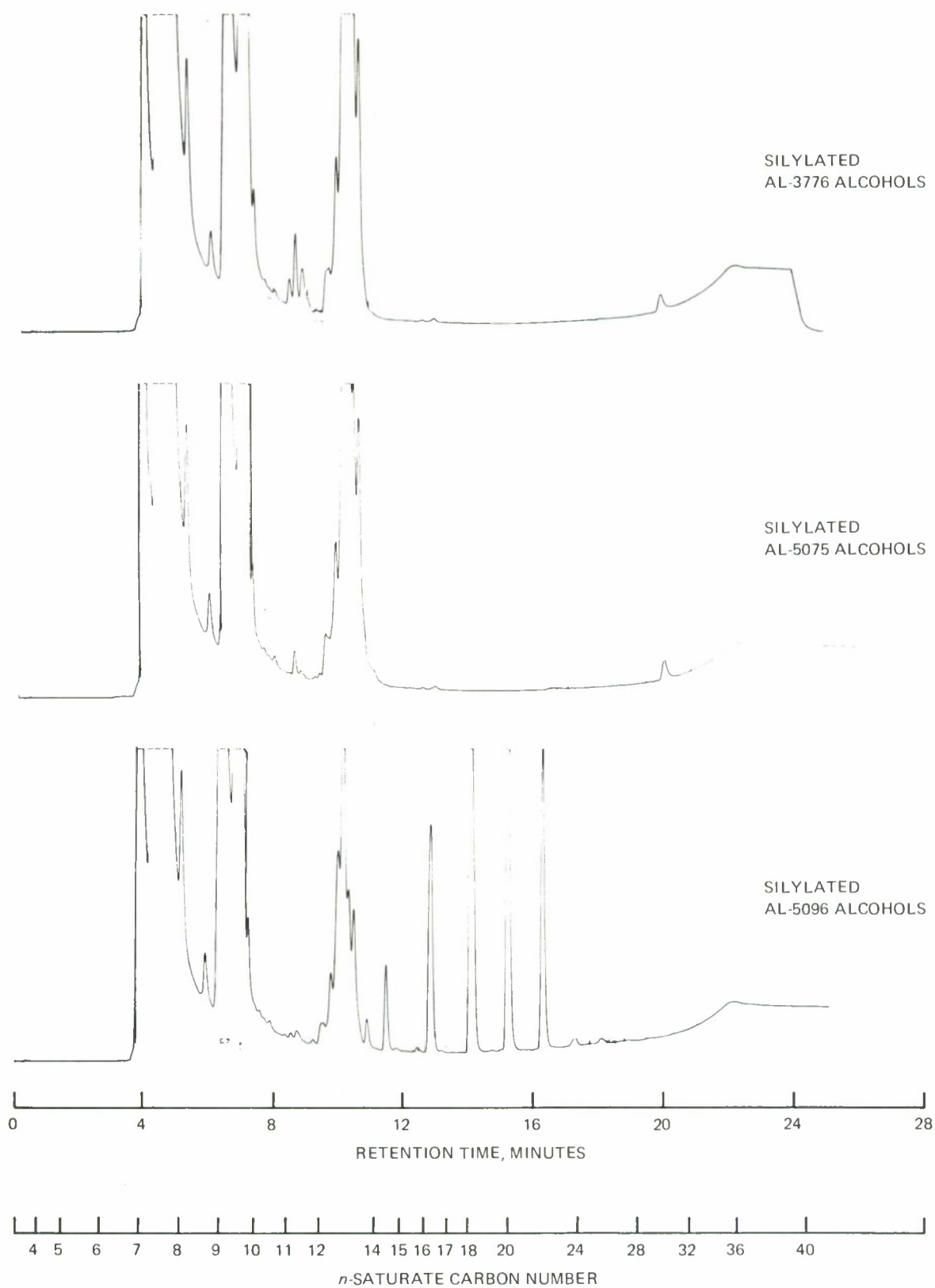


FIGURE 14. CHROMATOGRAMS OF SILYLATION PRODUCTS OF ALCOHOLS FROM THREE SYNTHETIC LUBRICANTS

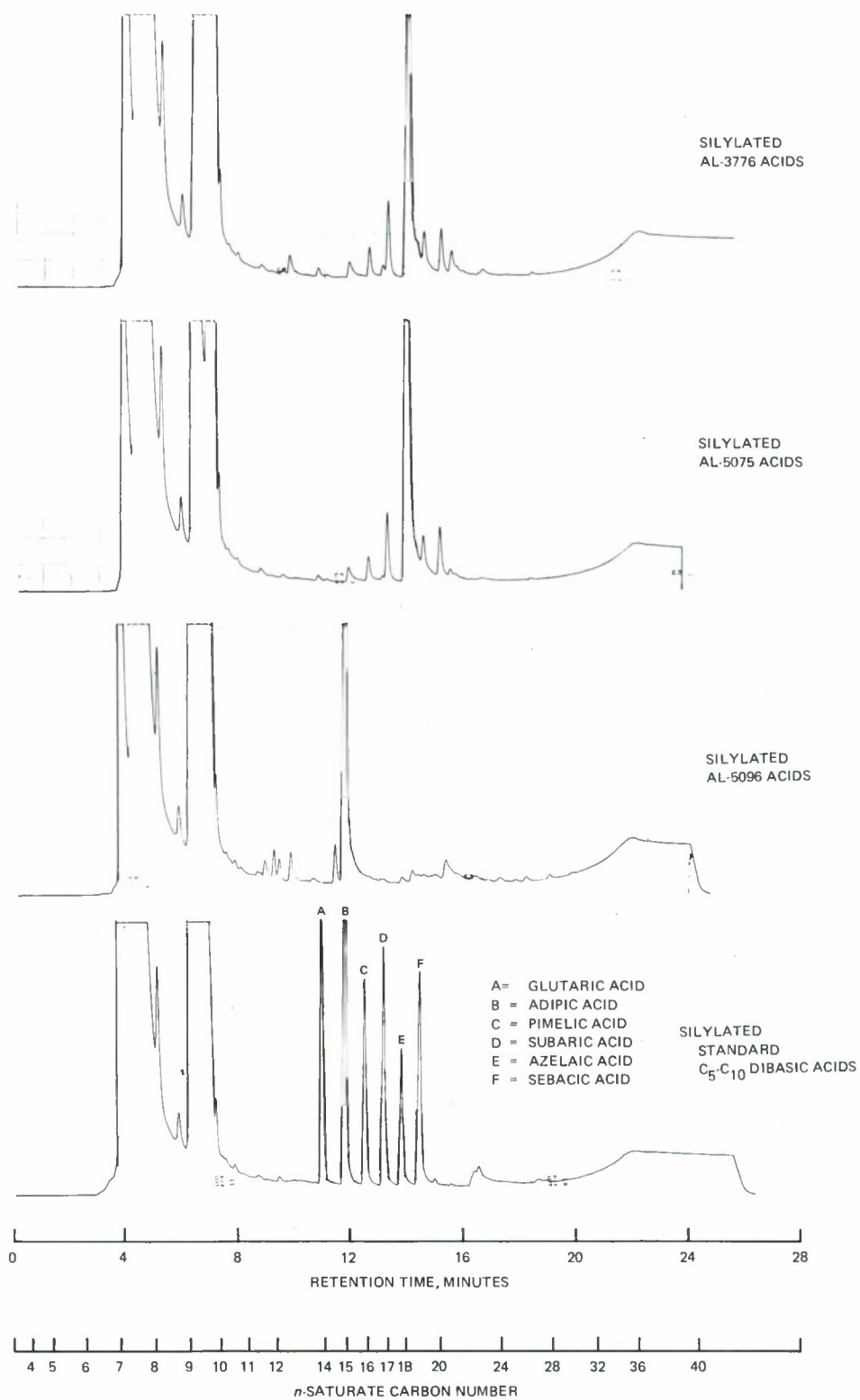


FIGURE 15. CHROMATOGRAMS OF SILYLATION PRODUCTS OF ACIDS FROM SYNTHETIC LUBRICANTS AND A STANDARD

TABLE 4. ANALYTICAL DATA FOR SOME ESTER BASED LUBRICANTS

	Lubricant Code No.						
	AL-3776	AL-5075	AL-5680	AL-5724	AL-F-1	AL-5096	AL-5594
Boiling Point Distribution ⁽¹⁾ , Percent Off, °C							
0.5	352	343	264	273	322	347	325
5	418	426	386	421	393	410	400
10	438	446	426	455	441	425	416
20	453	456	463	465	464	432	422
30	458	460	468	470	469	438	424
40	462	463	472	473	472	445	426
50	464	466	475	475	475	467	428
60	467	468	477	477	477	496	431
70	469	471	480	480	480	516	432
80	472	474	482	482	482	536	435
90	480	481	487	487	487	81/538	451
95	539	533	523	503	492		487
last/	95/539	96/539	95/523	96/528	98/539		99.5/539
Residue, % wt	5	4	5	4	2	19 ⁽²⁾	0.5
Lubricant Base Stock, % wt							
Ester	100	100	100	100	100	100	27 ⁽³⁾
Syn Hydrocarbon	--	--	--	--	--	--	73 ⁽⁴⁾
Mineral Oil	--	--	--	--	--	--	--
Other	--	--	--	--	--	--	--
Ester Alcohols, wt %							
Isoheptanol	--	--	--	--	--	--	--
2-Ethylhexanol	--	--	--	--	--	--	100
Iso-octanol (C ₈)	5	--	--	--	--	0.7	--
Isononanol (C ₉)	--	--	--	--	--	--	--
Isodecanol (C ₁₀)	95	98	--	--	--	38.9	--
Isoundecanol (C ₁₁)	--	--	--	--	--	--	--
Isododecanol (C ₁₂)	--	--	--	--	--	--	--
Isotridecanol (C ₁₃)	--	--	100	99	100	3.8	--
Other	--	2	--	1	--	56.6	--
Ester Acids, wt %							
Succinic (C ₄)	1.5	--	--	--	7.9	1.6	--
Glutaric (C ₅)	0.6	--	4.2	--	53.4	0.3	--
Adipic (C ₆)	1.4	1.2	95.8	100	35.6	87.1	--
Pimelic (C ₇)	1.8	1.4	--	--	--	--	1.9
Subaric (C ₈)	4.9	3.8	--	--	2.8	0.4	4.1
Azelaic (C ₉)	75.0	82.9	--	--	--	0.3	87.8
Sebacic (C ₁₀)	4.9	4.7	--	--	--	--	2.0
Other C ₁₁ + C ₁₂	9.9	6.0	--	--	0.3	10.3	4.2

(1) Note: Last % off plus residue equals 100% wt.

(2) Note: 6% off boiling above 569°C.

(3) Note: HPLC determined value of 27% wt compared to 25% wt determined by method of additions using infrared spectrometry with iso-octane as a diluent.

(4) Note: Composed of 3% wt C₂₀, 86% wt C₃₀, 9% wt C₄₀ and 2% wt C₅₀ oligomers of decene-1.

2. Methods to separate lubricants into component parts according to chemical types in order to simplify the subsequent analysis and identification of the component parts have been applied with favorable results.
3. It is possible to qualitatively and quantitatively analyze the major base stock components in hybrid lubricant blends, i.e., blends of synthetic hydrocarbons, esters, and mineral oils.
4. The synthetic hydrocarbon and alkyl diester portions of hybrid synthetic lubricants can be separated and analyzed by spectroscopy, gas chromatography, and high performance liquid chromatography.
5. Ester fractions of lubricants have been analyzed by gas chromatography after hydrolysis and derivatization to determine exact composition of the acidic and alcoholic components.
6. Gas chromatography methods have been applied to provide boiling point distribution of neat and separated fractions of lubricants.

RECOMMENDATIONS

1. Devise completed scheme and develop methodology for complete additive package characterization.
2. Define limiting ability to characterize other sources of lubricant base stocks not evaluated in this program (including re-refined oils, hybrid re-refined/virgin mineral oil blends) and devise schemes for their characterization.
3. Develop methodology for quantitating high performance liquid chromatographic techniques which are now limited to qualitative fingerprinting or gravimetric preparative collection of effluent.
4. Improve high temperature gas chromatographic resolution for more selective fingerprinting of hydrocarbons boiling above 800°F.
5. Investigate the use of combined gas chromatography-mass spectrometry for characterizing lubricant base stock and additives.

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APPENDIX A

Derivitization Procedure

Acids and alcohols are prepared for gas chromatographic analysis by derivitization. An approximately weighed 0.010 g sample is placed in a desiccator dried, 3 ml Reactivial (Pierce Chemical Company) and sealed using Teflon® rubber laminated discs in the Reactivial caps. The following Pierce Chemical Company supplied derivitization solutions were evaluated:

- (1) Tri-Sil®-Z
- (2) Methyl Alkyl-8™
- (3) Tri-Sil®/BSA, in dimethylformamide
- (4) Tri-Sil®/BSA, in pyridine

Several derivative solutions (identified by trade name) were evaluated initially in this program. Methyl Alkyl-8 treatment of a standard n-C₇-C₁₀ alcohol blend did not give sharp peaks nor was the reaction completed in the 30 minute heating period at 140°F. The other three derivitization solutions performed well except for solvent overlap with the n-C₇ alcohol in the case of Tri-Sil®-Z, characterized in the chromatograms in Figure A1. The upper two chromatograms were obtained with Tri-Sil®/BSA in each of two solvents; dimethylformamide and pyridine, the latter being chosen for routine use. All three of the Tri-Sil® solutions were satisfactory for acid silylation.

The Tri-Sil®/BSA in pyridine was selected for routine use based on chromatographic selectivity and ease of use. One mililiter pre-scored ampule of the derivitization solution was used for each sample. The top of the ampule was simply broken off and the solution poured into the sample container, shaken for 30 seconds, heated in 140°F water for thirty minutes, and then analyzed by gas chromatography. The peaks attributed to the alcohol or acid compounds are normalized to 100%.

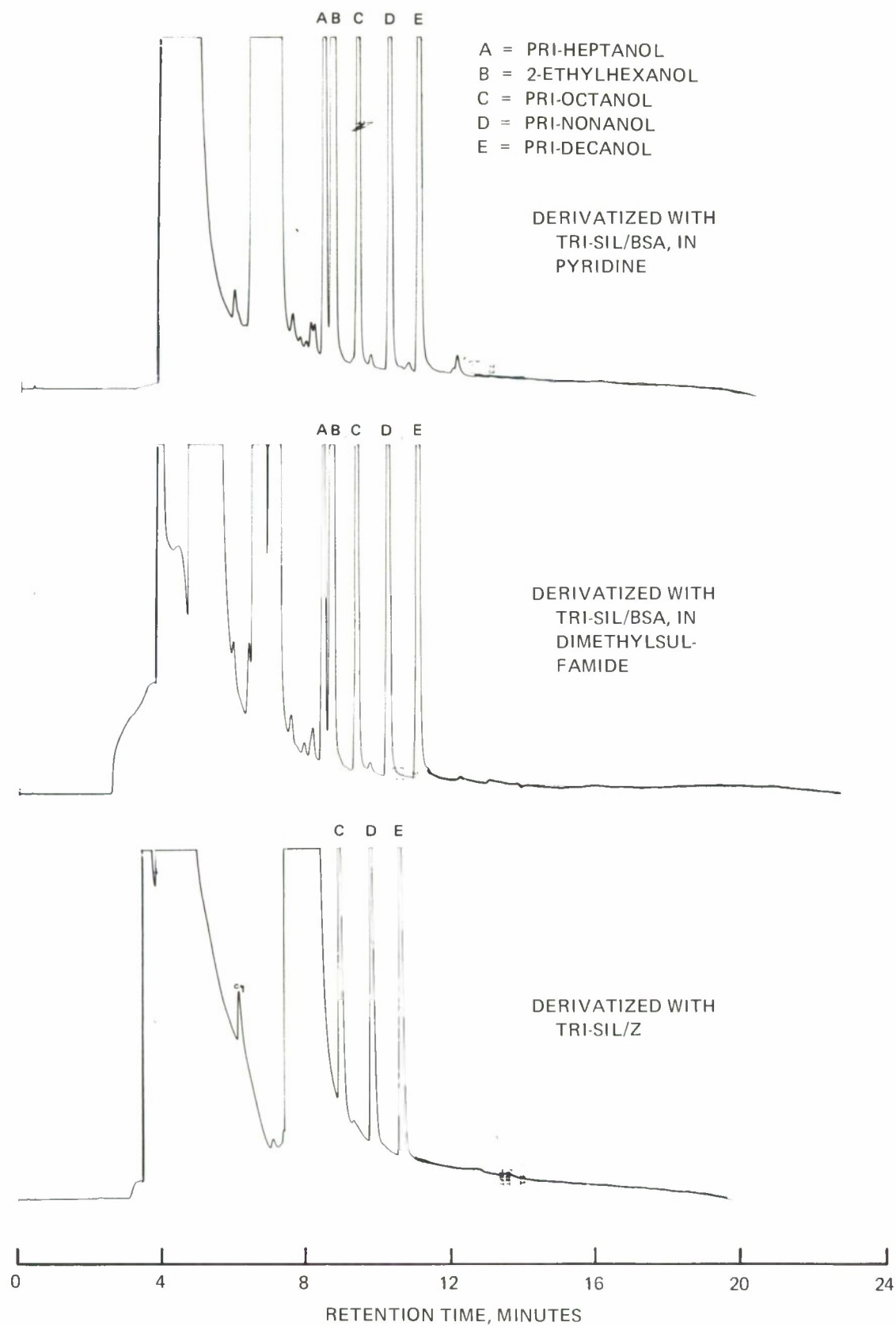


FIGURE A1. CHROMATOGRAMS OF THREE DERIVATIZATION PRODUCTS OF AN ALCOHOL STANDARD

APPENDIX B

Gas Chromatography Methods

Two gas chromatography methods have been developed for evaluating high boiling hydrocarbons, and are discussed below in addition to the data reduction procedures.

(1) Mineral and Crude Oil Procedure

The injection port for this system is an air-cooled 6-inch movable, pyrex glass hair packed, port with water jacket cooled septum. Sample is syringe injected into the glass hair at a point 2-1/2 inches from the septum face. The port is then pushed into a 3-inch heated jacket at 325°C and after 3 minutes the port is pulled back to the air-cooled position. The water jacketed inlet septum holder acts as a retainer when the port is pushed into the heated jacket. Approximately 3 inches of the port is in the heated jacket when the port is in the air-cooled position. The movable injection port is connected to a four feet x 1/8-inch stainless steel column coiled in the column oven. A second column in the oven is used to provide dual column-dual detector (hydrogen flame ionization) operation to compensate for column bleed. The columns are packed with 10% Dexsil 300 on Chromosorb P, AW 45/60 mesh. The column oven is held at 0°C for 2 minutes and then programmed to 450°C at 15°C/min and held at 450°C for 5 minutes. An Altamont crude oil (obtained from the Bureau of Mines, Bartlesville, Oklahoma) diluted in carbon disulfide provides *n*-saturate peak identification to n-C₆₀. Additionally, a special C₃-C₄₀ normal saturate standard (Table B1) is used for calibrating

TABLE B1. BOILING POINT
DISTRIBUTION STANDARD
(Note: The following solution
is diluted with carbon disulfide
in the ratio 1:3.)

<u>Carbon Number</u>	<u>Amount Per 100ml</u>
3	add to desired level
4	add to desired level
5	10.8
6	2.7
7	5.4
8	5.4
9	10.8
10	5.4
11	5.4
12	21.6
14	10.8
15	5.4
16	10.8
17	5.4
18	1.8g
20	1.8g
24	1.1g
28	0.7g
32	0.7g
36	0.7g
40	0.4g

the Hewlett-Packard laboratory data system (Model 3352-B) boiling point distribution method. Samples (5 grams) are prepared with a C₉-C₁₁ internal standard, 20% wt, in a 10 ml volumetric flask and brought to volume with carbon disulfide. Injection volume is 2 microliter. The C₉-C₁₁ internal standard is prepared by the addition of 5.0 g each of 99+% pure n-nonane, 4-methylnonane, n-decane, 2-methyldecane, and n-undecane in a proper storage container.

(2) Synthetic Lubricant GC Procedure

The injection port for this system is a dual, water-cooled, septum port for on column injection. The first inch of the columns are packed with pyrex glass hair into which the syringe injection occurs. The columns are six feet x 1/8-inch O.D. and are packed with 5% SE-30 on 45/60 mesh Chromosorb, AW-DMCS. The column oven is programmed from 0°C to 350°C and held 2 minutes. The *n*-saturate calibration standard in Table B1 is used for this system. Since the upper sample temperature limit of this system is 1000°F for the sample, mineral oils are generally not evaluated by this method. Synthetic lubricants generally contain mostly base material boiling below 1000°F. High molecular weight polymers are retained in the column as residue. Sample preparation is the same as in the above procedure. Injection volume is 1 microliter.

Both electronic integrators and on-line computers are used for detector output monitoring and signal evaluation. The software for boiling point distribution (both direct and by internal standard) using electronic integrator data obtained at 10 sec intervals and stored on punched tape was written in Xtrand and is used by telephone to Tyme-Share Incorporated by accoustical coupler hook-up.

The laboratory data system boiling point distribution requires on-line hook-up through an A/D converter and is limited to the software which is basically ASTM D2887 formatted. When internal standards are placed in a sample, operator interpretation of the boiling point distribution can give sample boiling point distribution and residue quantity.

Only the laboratory data system is used for peak analysis such as peak detection and normalization. When desired, both the electronic integrator and one or more laboratory data system A/D converters are hooked to the GC detector electrometer for multiple method analyses.

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